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SYNTHESIS OF AROMATIC POLYIMIDES FOR USE AS SOLID SORBENTS

by

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16. ABSTRACT

High surface area, highly sorbent, polyimide powders designed to replace or complement Tenax® G-C were obtained in high yield from pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenylsulfone (DADS), by precipitation polymerization in tetrahydrofuran (THF) solvent. The intermediate polyamide-acid powders were cyclodehydrated to high BET surface area (25-50 m^2/g) polyimide powders by slowly heating to 230-240 C in an evacuated rotary evaporator. About 40 weight percent of the powder was in the 200-500 μm particle diameter range desired for sorption sampling of vapor-phase organics. The polyimide powders are obtained as 0.01-1.0 μm diameter, loosely agglomerated, platelets and rod-like particles. Preliminary evaluation of the powder sorption/desorption characteristics with benzene vapor shows them to have greater capacity than Tenax but to have less desirable breakthrough characteristics due to slower sorption kinetics ascribed to inadequate connecting pore volume. However desorption occurs smoothly and quantitatively at 100 C.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The concentration of toxic organic vapors in ambient air may be as low as a few nanograms per cubic meter and still have biological consequences. Consequently the determination of human exposure to toxic organic compounds is an area of increasing importance to EPA. Since analytical techniques are not sensitive enough for *in situ* detection, pre-concentration of the sample is necessary. Tenax GC, the most widely used sorbent for the collection of volatile toxic organics from air, has been shown to lack selectivity for certain classes of lower molecular weight organics and has been shown to produce artifacts. The present investigation was undertaken to synthesize and characterize three different polyimide solid sorbents that would either replace or complement Tenax GC for the collection of toxic organic vapors from ambient air.

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ABSTRACT

Three new porous polyimide sorbent powders were prepared and characterized. These powders were prepared and studied for possible use as replacements for, or to complement, Tenax GC for the collection of toxic organic vapors from ambient air. The polyimide powders were prepared by condensing pyromellitic dianhydride (PMDA) with each of three different aromatic diamines, either in tetrahydrofuran (THF) or in N-methyl pyrrolidone (NMP) solvents. The three diamines were 4,4'-diaminodiphenylsulfone (DADS); 2,6-dichloro-p-phenylenediamine (DCPDA); and 4,4 diaminodiphenylmethane (DADM). The polymers made in THF precipitate as high surface area powders during the first stage polyamide-acid formation. The polymers made in NMP remain in solution at the polyamide-acid stage and are recovered as powders by nonsolvent precipitation. The polyamide-acid powders are then converted to polyimide powders by heating to 230-240 C while tumbling under vacuum (rotary drier). The polyimide made from PMDA/DADS in THF had the best properties, including the following:

- Polymer yield - 97 to 99 percent of theory
- Thermal stability - stable to 250 C
- Particle size distribution - 40 percent of product 200-500 μm
- Surface area - 26 to 50 m^2/gm
- Sorption characteristics - preliminary tests with benzene indicate substantially greater sorption capacity than Tenax but poorer sorption kinetics, resulting in early breakthrough
- Desorption characteristics - efficient (100 + 3 percent) recovery of sorbed benzene at a moderate temperature (100 C)

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CONTENTS

Foreword iii
Abstract iv
Tables vi
Figures. vii
Abbreviations and Symbols. viii
Acknowledgment ix

1. Introduction. 1
2. Conclusions 2
3. Recommendations 6
4. Discussion of Experimental Results. 8
    Monomer Purification/Purity. 8
        Polyamide-Acid Synthesis in Tetrahydrofuran 10
        Polyamide-Acid Synthesis in N-Methylpyrrolidone . . 10
        Recovery of Solution (NMP) Polymers 12
        Polymer Yield 15
        Polymer Solution Viscosity and Molecular Weight . . 16
    Cyclodehydration to Polyimides 19
    Polyimide Characterization 19
        Thermogravimetric Analysis. 19
        Particle Size 30
        BET Surface Area. 30
        Sorption Characteristics. 32
    Reproducibility Assessment 41
References 45

TABLES

Table		Page
1	Monomer Purification/Purity of Pyromellitic Dianhydride and Three Diamines	9
2	Polyamide-Acids Based on Pyromellitic Dianhydride and Three Diamines in THF--Yields and Molecular Weights.	11
3	Polyamide-Acids Based on Pyromellitic Anhydride and DADS in NMP--Yields and Molecular Weights.	13
4	Thermogravimetric Analysis of Polyimides	17
5	Polyimides Made in THF--Particle Sizes and Surface Areas . .	18

FIGURES

Figure		Page
1	Thermogram of DADS/PMDA Polyimide--Polymer No. 1	20
2	Thermogram of DADS/PMDA Polyimide--Polymer No. 2	21
3	Thermogram of DADS/PMDA Polyimide--Polymer No. 3	22
4	Thermogram of DADM/PMDA Polyimide--Polymer No. 4	23
5	Thermogram of DADM/PMDA Polyimide--Polymer No. 5	24
6	Thermogram of DADM/PMDA Polyimide--Polymer No. 6	25
7	Thermogram of DCPDA/PMDA Polyimide--Polymer No. 7.	26
8	Thermogram of DCPDA/PMDA Polyimide--Polymer No. 8.	27
9	Thermogram of DCPDA/PMDA Polyimide--Polymer No. 9.	28
10	Vapor Breakthrough Characteristics for Several Candidate Resins Compared to Tenax GC.	33
11	SEM Photomicrograph of DADS/PMDA Polyimide 1	35
12	SEM Photomicrograph of DADS/PMDA Polyimide 2	36
13	SEM Photomicrograph of DADS/PMDA Polyimide 10.	37
14	SEM Photomicrograph of DADS/PMDA Polyimide 14, Precipitated with Acetone.	38
15	SEM Photomicrograph of DADS/PMDA Polyimide 10, Precipitated with Acetone.	39
16	SEM Photomicrograph of DADS/PMDA Polyimide 10, Precipitated with Water.	40
17	SEM Photomicrograph of DADS/PMDA Polyimide 10, with IO Percent Urea, Precipitated with Acetone.	42
18	SEM Photomicrograph of DADS/PMDA Polyimide 10, with IO Percent Urea, Precipitated with Water.	43

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

PMDA	=	pyromellitic dianhydride
DADS	=	4,4'-diaminodiphenylsulfone
DCPDA	=	2,6-dichloro-p-phenylenediamine
DADM	=	4,4'-diaminodiphenylmethane
MDA	=	methylenedianiline
BET	=	Brunauer-Emmett-Teller; authors of a physical adsorption isotherm
GC	=	gas chromatography
DMAC	=	dimethyl acetamide
TGA	=	thermogravimetric analysis
NMP	=	N-methylpyrrolidone
SEM	=	Scanning electron microscope

SYMBOLS

M_v	=	molecular weight determined by viscosity measurement
T_G	=	glass transition temperature
ρ	=	bulk density of the packed bed, g/cm^3

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SECTION 1

INTRODUCTION

Hazardous organic vapors may be present in air at concentrations as low as a few nanograms per cubic meter and still present a potential biological threat. Preconcentration of such vapors is thus necessary in many cases to provide sufficient sample for accurate air analysis. The available methods for preconcentrating vapor-phase organics include the use of sorbent cartridges, cryogenic systems and solvent impingers. These methods, and their characteristics, have been discussed by Pellizzari et al. in prior work for the Environmental Protection Agency.[1] As discussed by these workers, preconcentration using porous polymeric sorbents has been the most successful and useful procedure. Tenax GC is the most used and most versatile sorbent commercially available at present.

However, Tenax GC (porous powder poly-2,6-diphenyl-para-phenylene oxide) has several performance deficiencies that would be very desirable to correct. These include low retention and breakthrough volumes for high volatility organic compounds. In fact, the more polar volatile organics such as acrylonitrile and acetonitrile, vinyl chloride, methylene chloride, acrolein, propylene oxide, and the like cannot be adequately analyzed using Tenax GC. In addition, Tenax GC is subject to high background, or column bleed, due to slow release of prior adsorbed compounds, or slow thermal breakdown of the polymer structure. Also, the elution of artifact peaks, either as a result of chemical reaction of adsorbing species on Tenax GC[1,2], or possibly due to displacement desorption of prior adsorbed species[3], is a particular problem.

Consequently, it is desired that new sorbent materials be developed that are superior to Tenax GC in as many of the following properties as possible:

- Greater adsorption capacity for the more volatile vapor-phase organics
- Greater selectivity in adsorption and thermal release of multiple pollutants
- Improved thermal properties (i.e., minimal background or bleed contribution to eluted volatiles for analysis)
- Minimal artifacts formed during collection of reactive organic compounds
- Low water vapor retention
- Resistance to reactive inorganic gases such as ozone, NO_x and SO_x.

SECTION 2

CONCLUSIONS

Straightforward, practical procedures have been developed for the purification of all four monomers (PMDA, DADS, DADM, DCPDA, abbreviations on page viii) to 99.9+ percent purity. These monomers are usable to reproducibly prepare the three desired polyimides as their fine-particle-precipitated polyamide-acid precursors in tetrahydrofuran. Total polymer yields, as desired, met or exceeded 100 grams from three polymerizations of each monomer pair (from polymerizations of DADS/PMDA). The molecular weights of the polyamide-acid intermediate polymers were consistent with those reported by prior workers(1), with the DADS polymers reaching M_V = 7,000; DCPDA polymers reaching M_V = 3,000 and DADM polymers reaching M_V = 10,700.

The polyamide-acids were readily cyclodehydrated, in dry powder form, to the polyimides. Based on TGA results, the polyimides are all stable to ~250 C, with only minor weight losses of 1-3 weight percent attributable to physical losses of water and adsorbed solvents. Above ~250 C the weight losses continue, at an accelerated rate, indicating chemical changes are occurring. The upper limit for prolonged use of the polyimides probably lies somewhere between 250 and 300 C. The upper useful temperature range should be determined.

The polyimides are recovered after the cyclodehydration as powders, which in two cases (DADS and DCPDA polyimides) are recovered with appreciable fractions in the desired particle size range of 200-500 μm. It is likely that the percentage of this particle size fraction can be increased by manipulating certain polymerization variables, such as PMDA addition rate and the reaction temperature/time cycles, and by standardizing and controlling the powder handling and size classification procedures.

The surface areas of the DADS/PMDA polyimides made in THF are the highest obtained and are consistent, or reproducible, to a very substantial degree in successive polymerizations. The actual values obtained range from 26 to 50 m^2/g. The average (and mean) values are 34 m^2/g. These values appear to be greater than those found for the standard commercial product Tenax GC (25 m^2/g). However the experimental error in measurement may be as great as ± 50 percent so that 34 + 17 m^2/g and 25 + 12 m^2/g is perhaps a more correct way to express the results, showing that they do not differ to a statistically significant degree. SEM photomicrographs of these products show that the most promising are probably combinations of stacked plates, or platelets, ranging in size from about 2-5 μm across to 0.01-1.0 μm in thickness, and rod-like, or precursor microfibril, particles of a similar submicron diameter. The macroscopic particles are agglomerates of these basic structures, which contain appreciable random micron and submicron void volume. Consequently the high surface areas of the particles can probably be largely attributed to these interconnected voids. It is concluded that the actual areas obtained are probably a function of the sizes of the particles, the ratio of microfibrils to platelets and the degree to which

they are agglomerated (i.e., fused together). It appears that the rods, or microfibrils, are favored at higher molecular weights.

Powders with higher and more nearly reproducible surface areas probably can be prepared by:

- Controlling certain polymerization variables such as
  - -- Rate of PMDA addition to the reactor
  - -- Reaction time/temperature profile
- Producing polymers with higher molecular weights
- Controlling the size of the microfibrils and their degree of agglomeration.

The DADS polyimides made in NMP (solution polymerization) show very low surface areas (<1 m^2/g). Although the reason for this is not known with certainty at present, it appears likely to be due to a combination of factors, including the nature of the polyamide-acid precipitation process from true solution in a polar solvent, the effect of relatively low molecular weight polymer chains on this process, and possible retention of small amounts of NMP by the fine particle product after washing and drying. Immediately after precipitation the products qualitatively appeared to have high surface areas (flocculate white precipitates). After the precipitates were carefully washed (with acetone and/or water) to remove NMP, they were either vacuum dried at room temperature or freeze dried from a frozen water slurry. During this drying process a considerable amount of agglomeration invariably occurred. Then, during cyclodehydration up to 230 C, the products further agglomerated to very large particles or even flake or sheet material. These products had, as indicated, surface areas of <1 m^2/g.

Decided improvement was obtained when DADS/PMDA Product 10, made in THF, was dissolved in NMP and recovered by precipitation using the same procedures. Precipitation with acetone or water yielded polyimide powders with 2 m^2/g and 4 m^2/g, respectively, when the products were not heated above room temperature during washing and were freeze-dried from a frozen water slurry. It is likely that the higher molecular weight of Product 10 is the reason for this improvement. Although the actual surface areas were still disappointingly low, this does indicate that if the desired higher molecular weight polyamide-acids can be achieved by solution polymerization of DADS and PMDA, further increases in surface area can be expected. It is also considered likely that the precipitation procedure itself (e.g., polyamide-acid solution concentration, method and rate of combining polymer solution and nonsolvent, and the like) will affect the ultimate surface areas obtained.

Addition of 10 weight percent urea (relative to polyamide-acid) to a DADS/PMDA Polymer 10 solution in NMP, followed by precipitation and recovery of the product using the same procedures, resulted in a further, relatively large, increase in surface area when acetone was the nonsolvent (14 m^2/g). However, the nature of the precipitated polymer (porous polymer beads or spheres) was quite different from the products obtained in the THF precipitation polymerization process. Precipitation with water gave a powder physically more like the high surface area powders from the THF precipitation polymerization, but the

surface area has not yet been measured due to experimental problems. The surface area probably will vary as a function of urea concentration. Again, polymer molecular weight and solution concentration, as well as precipitation and leachate extraction procedure, would be expected to affect surface area. It is thus likely that manipulation of these variables will produce polyimide powders with a range of surface areas. However, it is not possible to estimate the highest level of surface area attainable without further work.

The DADM and DCPDA polyimides made in THF have substantially lower surface areas and are considered unlikely to be good sorption candidates.

In prior work for the U.S. Environmental Protection Agency, Pellizzari et al.(1), have shown that three aromatic polyimides have particular promise for solving the problems and meeting the criteria listed in Section 1 for a sorbent to replace or supplement Tenax GC. The retention volumes of selected volatile organics on these polyimide sorbents were shown to be one to two orders of magnitude greater than on Tenax GC. Breakthrough data on these experimental sorbents were reproducible and showed improvement over Tenax GC. Both background and artifact production were reduced.

The polyimides studied were the reaction products of pyromellitic dianhydride (PMDA) and three aromatic diamines: 4,4'-diaminodiphenyl-sulfone (DADS); 2,6-dichloro-p-phenylenediamine (DCPDA); and 4,4'-diamino-diphenylmethane (DADM), also known as methylenedianiline (MDA). These products were prepared in tetrahydrofuran (THF), a moderate polarity solvent for the PMDA and diamine monomers, but a nonsolvent for two of the three intermediate stage products (polyamide-acids) which are first produced and isolated as dry powders. The DCPDA polyamide-acid stays in solution because of the very low molecular weight product obtained. THF was used because the intermediate polyamide-acids were then easily and directly obtained as relatively high surface area powders and because it is readily evaporated or extracted from these products. The final polyimides were then produced by solid state thermal cyclodehydration of the polyamide-acid powders at temperatures up to 230 C.

The basic objectives of this study were:

- To prepare 100-gram quantities of three aromatic polyimides (based on pyromellitic dianhydride and three commercially available aromatic diamines: 4,4'-diaminodiphenylsulfone; 2,6-dichloro-p-phenylenediamine; and 4,4'-diaminodiphenylmethane), each in approximately 33-gram batches, using tetrahydrofuran (THF) as the polymerization solvent.

- To determine batch-to-batch variability of the polylers made in THF as measured by solution viscosity, molecular weight, thermogravimetric analyses (TGA) and BET surface area measurements, with the goal of substantially reproducing the properties of each polyimide in each of the three batches made.

- To prepare controlled molecular weight polyimides with nonpolar, nonwater-adsorptive end groups from the same monomers in THF.

- To prepare substantially higher molecular weight polyimides from these monomers than have been obtained in prior work by conducting polymerizations in a true solvent for the polyamide acids, N-methylpyrrolidone (NMP).

- To produce polyimides with substantially increased surface areas designed to provide greater organic pollutant adsorption capacity by combinations of carefully controlled insolubilization procedures, including coprecipitation and later extraction of solvent leachable phases, and cyclodehydration (imidization procedures).

SECTION 3

RECOMMENDATIONS

It is recommended that about 100 grams of DADS/PMDA polyimide be made following the THF precipitation procedures used to synthesize Product 10 in the present work. The polyamide-acid should be made in three approximately equal-sized batches, in THF, using freshly purified DADS and PMDA. This will determine the reproducibility of the synthesis procedure. The intermediate polyamide-acids should be characterized by viscosity molecular weight. The powder products should be carefully, uniformly and slowly vacuum cyclodehydrated (heating rate 60 C/hour, to 230 C). The polyimide powders should then be carefully size-classified to maximize the yield of 200-500 μm diameter particles (60/80 mesh fraction), since this macroscopic size is the optimum for packing sorbent columns. The polyimide powders should then be characterized by thermogravimetric analysis (TGA) and the BET surface area technique. Assuming the three batches of polyimide are comparable, they should be composited for laboratory and field sorption studies. In this study a carefully selected set of potentially hazardous volatile organic compounds should be studied in terms of their sorption/desorption characteristics on the experimental DADS/PMDA polyimide powders, in comparison with Tenax GC and Spherocarb®.

Further study of the solution polymerization and controlled precipitation preparation of DADS/PMDA polyimide powders should be held in abeyance, pending the outcome of the above recommended study. As shown in the CONCLUSIONS, there is good reason to believe surface areas of ≥ 14 m^2/g can be attained via this route but the results so far obtained do not guarantee that values of >34 m^2/g can be achieved. If further work is to be done in solution, it could include any, or all, of the following areas with the variables indicated:

- Further studies of NMP solvent purification and drying
- Purification/drying of DMAC as an alternative solvent
- Polymerization of freshly purified PMDA and DADS in these solvents
  - Polymerization temperature and heating rate
  - Rate of PMDA addition
  - Use of tertiary amine catalysts
- Polyamide-acid precipitation and recovery
  - Polymer concentration
  - Nonsolvent (acetone or water) addition rate/agitation procedure
  - Urea concentration

- Polymer precipitate recovery/solvent removal with water or acetone

  - Sequential wash procedure (dilute/centrifuge/decant)
  - Continuous aqueous dialysis
  - Controlled temperature Soxhlet extraction
  - Freeze dry (water)

- Cyclodehydration (rotary vacuum drier)

  - Control heating rate (possible isothermal stages)
  - Control tumble (turning) rate
  - Vacuum.

The objective of any additional solution polymerization work to be proposed or undertaken would be to obtain higher molecular weight polyamide-acids and to obtain high yields of 200-500 μm particle-size DADS/PMDA polyimide powders with surface areas ≥ 34 m^2/g.

SECTION 4

DISCUSSION OF EXPERIMENTAL RESULTS

MONOMER PURIFICATION/PURITY

Four monomers of high purity (>99.9 percent pure) were required to prepare the polyimides. These included one aromatic dianhydride, pyromellitic dianhydride (PMDA), and three aromatic diamines, including the following: 4,4'-diaminodiphenylsulfone (DADS); 2,6-dichloro-p-phenylene-diamine (DCPDA); and 4,4'-diaminodiphenylmethane (DADM). The highest purity PMDA identified commercially was a 99.2 percent pure, off-white solid, melting point ~270 C, obtained from Polysciences, Warrington, PA. White, powdery DADS of ~99 percent purity, melting point ~175 C, and tan, flaked solid DADM of ~97 percent purity, melting point ~89 C, were obtained from Aldrich Chemical Co., Milwaukee, WI. Black powdery, highly impure DCPDA (purity ~70-80 percent) was obtained from K&K, Inc., Division of ICN Pharmaceuticals, Inc., Plainview, NY.

PMDA was purified both by vacuum sublimation and, in a refined procedure giving higher purity monomer, by recrystallization from reagent grade acetic anhydride, followed by sublimation. DADS and DADM were purified by vacuum sublimation for Experiments 1-6. The DADS for Experiments 10 through 14 was purified by recrystallization from deaerated (oxygen-free) methanol, since it was found this procedure more easily produced a higher purity monomer than sublimation. DCPDA was purified by vacuum sublimation, followed by recrystallization from carefully deaerated reagent grade methanol, then by a final vacuum resublimation. Repeated sublimations of crude DCPDA yielded an inferior product. Aniline was distilled and dried over molecular sieve 3A.

The melting point and purity data on the purified monomers are summarized in Table 1. The monomers are listed in this table according to the polymerization experiments in which they were used. There were, as shown by Table 1, a total of eleven polymerizations carried out from which useful products were obtained. One DCPDA/PMDA polymerization, using thrice sublimed DCPDA and once sublimed PMDA, is not included in the table because the total polymer yield was very low (<10 percent), presumably due to the relatively low purity of the DCPDA. The yellow needles obtained by this purification procedure melted at ~122 C, as opposed to the sharp 124.5 C melting point recorded in Table 1 for very pale yellow needles obtained by the improved (i.e. sublimation, recrystallization, resublimation) purification procedure. The 124.5 C melting point corresponds to 99.99 percent purity by differential scanning calorimetry (DSC) analysis using the automated Mettler TA 3000 system.

All purities recorded in Table 1 were determined by DSC, according to the method used by Pellizzari, et al. (Reference 1, Volume 1, page 21), except the data for PMDA for Experiments 1 through 6. Those PMDA melting points were determined manually, using a sealed microcapillary of PMDA heated in a temperature

TABLE 1. MONOMER PURIFICATION/PURITY OF PYROMELLITIC DIANHYDRIDE AND THREE DIAMINES

No.	Diamine[a]	Purification Method[b]	Melting Point[c], C	Percent Purity[d]	Anhydride[e]	Purification Method[b]	Melting Point[f], C	Percent Purity[d]
1	DADS	1X sublimed	177.0	99.9	PMDA	1X sublimed	281-282	--
2	DADS	1X sublimed	177.0	99.9	PMDA	1X sublimed	281-282	--
3	DADS	1X sublimed	177.0	99.9	PMDA	1X sublimed	281-282	--
4	DADM	1X sublimed	92.5	99.9	PMDA	1X sublimed	281-282	--
5	DADM	1X sublimed	92.5	99.9	PMDA	3X sublimed	284-285	--
6	DADM	1X sublimed	92.5	99.9	PMDA	3X sublimed	284-285	--
7	DCPDA	1X recrystallized 2X sublimed	124.5	99.99	PMDA	2X recrystallized 1X sublimed	285.8	99.93
8	DCPDA	1X recrystallized 2X sublimed	124.5	99.99	PMDA	2X recrystallized 1X sublimed	285.8	99.93
9	DCPDA	1X recrystallized 2X sublimed	124.5	99.99	PMDA	2X recrystallized 1X sublimed	285.8	99.93
10	DADS	1X recrystallized	177.5	99.96	--	2X recrystallized 1X sublimed	285.8	99.93
11	DADS[g]	1X recrystallized	177.5	99.96	PMDA	2X recrystallized 1X sublimed	285.8	99.93

(a) DADS = 4,4'-diaminodiphenylsulfone
DADM = 4,4'-diaminodiphenylmethane
DCPDA = 2,6-dichloro-p-phenylenediamine.

(b) 1X = one time; 2X = two times; 3X = three times.

(c) Melting point of DADS and DADM determined by Perkin Elmer DSC-2 (1.25 C/min); DCPDA by Mettler TA 3000 system (programmed DSC, 2 K/min).

(d) Purity determined from DSC traces.

(e) PMDA = pyromellitic dianhyride.

(f) Melting point of 1X and 3X sublimed PMDA determined manually with sealed capillary in a calibrated Fisher melting point apparatus; 2X recrystallized and 1X sublimed PMDA determined by Mettler TA 3000 system as in (d).

(g) Aniline used in Polymerization 11 vacuum distilled and dried over molecular sieve 3A.

calibrated Fisher melting point apparatus. However, the Mettler TA 3000 system DSC was used to measure the melting point and purity of the PMDA of Experiments 7-15 (only 7-11 are recorded in Table 1). The measured melting point (285.8 C) equated to a purity of 99.93 percent. It is estimated that the purity of once sublimed PMDA is >99.5 percent and of thrice sublimed monomer is >99.8 percent.

Polyamide-Acid Synthesis in Tetrahydrofuran

The polyimide precursors (Polymer Nos. 1 through 11) were all prepared in dry, HPLC grade (Burdick and Jackson Laboratory, Muskegon, MI) tetrahydrofuran (THF), following the general procedure of Pellizzari et al.(1). Hence, a typical reaction used 46.63 grams of monomers (21.80 grams PMDA, 24.83 grams DADS) and 1200 cc of THF. The reactions were carried out in a flame-dried, 3-neck, 3-liter flask, fitted with a paddle-type Trubore® stirrer, a powder addition funnel and a reflux condenser, under a dry argon (passed through CaH_2 drying tower) atmosphere. Addition of the dry powder reagents was done using a separatory funnel fitted with a special, large bore (0.5-in. ID) stopcock for allowing powder flow. The powder addition funnel also had a bypass argon line so that argon was continually passed over the diamine and dianhydride powders to avoid any possible absorption of water vapor or oxygen. The anhydrous (dried over CaH_2) THF solvent was transferred to the reaction flask directly from the storage bottle, again using argon pressure to effect the transfer through a Pyrex glass connecting line. In this way neither solvent nor monomers were exposed to the atmosphere during addition to the reactor. The polymerizations were in each case carried out using the time and temperature conditions specified by the prior workers(1). The polymers were then recovered, also using the procedures specified earlier(1).

The polyamide-acid products in Experiments 1-6 and 10 and 11 precipitated from the polymerization solution as fine powders during the course of the polymerization. The DCPDA/PMDA products (Experiments 7-9) stayed in solution and had to be precipitated by adding reagent grade chloroform (Burdick and Jackson HPLC grade, distilled in glass). The polyamide-acid yield, inherent viscosity and molecular weight data for the polymerizations done in THF are summarized in Table 2. The final polyimide products obtained after cyclodehydration averaged 34 m^2/g in surface area. This is discussed later under BET surface area measurement.

Polyamide-Acid Synthesis in N-Methylpyrrolidon

Polymerization Experiments 12 through 15 were carried out in dry N-methylpyrrolidone solvent instead of in THF. This highly polar solvent dissolves the polyamide-acid polymer products, as well as the starting monomers. Hence, it was anticipated that higher molecular weight polyamide-acids would be produced, since the molecular weight limiting step of polymer precipitation, due to growing insolubility in THF as the polymer chain length increase, would be avoided. It was further anticipated that a higher molecular weight DADS/PMDA polyimide could be precipitated under controlled conditions to yield microfibrillar precipitates with higher surface areas than are obtainable by the precipitant polymerization procedure, using THF as the reaction solvent.

TABLE 2. POLYAMIDE-ACIDS BASED ON PYROMELLITIC DIANHYDRIDE AND THREE DIAMINES IN THF--YIELDS AND MOLECULAR WEIGHTS

Composition	Theoretical Yield, g	Actual Yield, g	Percent Yield	$[\eta]$ (a)	M_v (b)
1. DADS/PMDA	46.63	34.14	73.2	0.141	3,600
2. DADS/PMDA	46.63	43.50	93.3	0.135	3,400
3. DADS/PMDA	46.63	44.97	96.5	0.183	5,000
4. DADM/PMDA	41.64	38.56	92.6	0.202	5,700
5. DADM/PMDA	41.64	39.08	93.9	0.318	10,200
6. DADM/PMDA	41.64	39.23	94.2	0.329	10,700
7. DCPDA/PMDA (c)	30.62	3.02 (e)	9.9	0.076	1,600
8. DCPDA/PMDA (d)	43.90	5.22 (f)	11.9	0.079	1,700
9. DCPDA/PMDA (d)	32.12	5.75 (g)	17.9	0.123	3,000
10. DADS/PMDA	46.63	46.24	99.2	0.239	7,000
11. DADS/PMDA (h)	46.53	45.10	99.0	0.210	6,000

(a) Inherent viscosity in DMAC at 30 C (0.5 g/dl), after extraction with THF.

(b) Molecular weight (viscosity) estimated from $M_v = 4.42 \times 10^4 [\eta]^{1.28}$ (ref. 4).

(c) PMDA added to DCPDA/THF solution at 23 C.

(d) PMDA added to DCPDA/THF solution at 60 C.

(e) Product recovered in two fractions. Fraction 7a (3.02 g, after ether extraction/recovered by $CHCl_3$ precipitation from original solution. Fraction 7b (28.92 g) is the ether insoluble portion of the remaining product. Total ether insoluble product, a+b, is 28.92 g (94.4%).

(f) Fraction 8b (35.34 g), total ether insoluble product 40.56 g (92.4%).

(g) Fraction 9b (24.88 g), total ether insoluble product 30.63 g (95.4%).

(h) Repeat (10) with 5 mole percent aniline to provide a high concentration of N-phenyl imide end groups. That is, use 23.59 g (0.095 mole) DADS, 21.8 g (0.10 mole) PMDA, and 0.93 g (0.01 mole) aniline.

In order to carry out the solution polymerizations, NMP was purified and dried. Amide solvents, like NMP, which is a highly polar cyclic amide, are prone to contain small amounts of amine impurities and to also absorb or contain dissolved water. Both of these impurities will act to limit molecular weight by reacting preferentially with an equivalent portion of PMDA. Hence, the NMP (reagent grade, Aldrich Chemical) was first predried with a 3A molecular sieve to remove most of the water. It was then slowly vacuum distilled, under a residual argon atmosphere, from phosphorus pentoxide (P_2O_5) powder, which chemically reacts with both amines and water. A clear, colorless, center cut (about 75 percent of the total NMP distilled, bp 47.5-48.0 C) was collected in a flame-dried Pyrex round-bottom flask, and maintained under an anhydrous argon atmosphere until used.

The transfer of the NMP to the reaction flask and the reaction procedures used were the same as those described above for THF, except that higher solution concentrations (10-15 weight percent) were used since this is known to result in higher molecular weight polymers. The polymerizations were carried out by adding the PMDA to the DADS dissolved in the NMP at ambient temperature, then raising the reaction temperature to 65-68 C to drive the polymerization to yield higher polyamide-acid molecular weights. The yield and molecular weight data for these products are recorded in Table 3.

Recovery of Solution (NMP) Polymers

Polymer yields of the solution DADS/PMDA polyamide-acids were determined by precipitating a 5-10 cc aliquot in a large excess of THF (10-20 volumes THF to NMP solution), centrifuging and washing the product with THF, then with diethyl ether, and vacuum drying. A 0.5-gram portion of this product was then used to determine molecular weight by solution viscosity in DMAC, as described later. The data are listed in Table 3.

Recovery of the products was studied by each of the following procedures:

(1) Slow addition of cold (0 C), dry THF to well-stirred, cold (0 C), NMP solution of polyamide-acid

(2) Reverse addition of (1), i.e., NMP solution, to THF

(3) Slow addition of cold (0 C) dry acetone to well-stirred, cold (0 C) NMP solution of polyamide acid

(4) Reverse addition of (1), i.e., NMP solution, to acetone

(5) Repeat (1) with 10 percent by weight urea, based on DADS/PMDA polyamide-acid, added to NMP polymer solution

(6) Repeat (3) with 10 percent by weight urea, based on DADS/PMDA polyamide-acid, added to NMP polymer solution.

(7) Slow addition of room temperature acetone to well stirred, room temperature NMP solution of polyamide-acid.

TABLE 3. POLYAMIDE-ACIDS BASED ON PYROMELLITIC ANHYDRIDE AND DADS IN NMP -- YIELDS AND MOLECULAR WEIGHTS

Polymer Number	Theoretical Yield, g	Actual Yield[a], g	Percent Yield	$[\eta]$[b]	M_v[c]
12	46.63	45.1	96.8	0.170	4,600
13	46.63	46.1	98.8	0.182	5,000
14	46.63	46.0	99.0	0.192	5,200

(a) Determined by precipitating a 5-10 mL aliquot of NMP solution with a 10-20-fold excess of THF, washing the precipitate with THF and diethyl ether and vacuum drying at 50 C, to obtain approximately 1-gram samples of product. Yield determined by proportional calculation.

(b) Inherent viscosity in DMAC at 30 C (0.5 g/dl).

(c) Molecular weight (viscosity) estimated from $M_v=4.42\times10^4[\eta]^{1.28}$.

(8) Slow addition of room temperature water to well stirred, room temperature NMP solution of polyamide-acid.

The precipitations were carried out initially by precipitating small (1-2 mL, 0.1-0.2 g polymer) samples of Product No. 12 with large (~30-fold) excesses of nonsolvent. In these experiments, precipitating the DADS/PMDA polyamide acid using Procedures 1 through 4 showed that the best procedure was to add the nonsolvent slowly to the NMP solution (Procedures 1 and 3). The initially precipitated polymers had a somewhat microfibrillar (30X optical microscope) appearance. The precipitated polymer using the acetone (Procedure 3) was more fibrillar and less agglomerated than the THF precipitated product, although both products were combinations of fibrillar and irregular particle precipitates.

The use of the reverse procedures, 2 and 4, in which the NMP polymer solution was added to the nonsolvent, resulted in more clumping or agglomeration of polymer fibrils or particles. It was then found that the addition of room temperature acetone to room temperature NMP solution gave a better appearing product. That is, somewhat less agglomeration of precipitated microfibrils/particles appeared to occur. Hence, of the above listed six potential recovering procedures, the one chosen for recovering larger quantities of the NMP solution products was the addition of 10-20 volumes of room temperature acetone to rapidly stirred, NMP polymer solution, also at room temperature.

Water (distilled) was then also tried since it would be very convenient and is known to be an excellent NMP solvent, while being a nonsolvent for these polymers. One danger of using water is the potential for polymer hydrolysis. However, rapid precipitation of the polymer with water would yield a heterogeneous mixture and hydrolysis would be expected to be slow. Hence, water was also tried (procedure 8) and found to be a good candidate nonsolvent, giving a very fine, easily separated and recovered precipitate.

Samples were then precipitated from DADS/PMDA polyamide-acid Products 12-14 using both acetone and water to test this procedure for the recovery of sizable quantities (10 grams) of product. Even this minor scale-up resulted in agglomerated precipitates. Even when the precipitates were washed five times with acetone (or water, respectively) before starting the vacuum drying process at room temperature, the polyamide-acid products were partly fused sheets. It was found that the best procedure for recovering these products was to add sufficient water to the final washed, fine particulate product, to form a fine slurry, to freeze it and to freeze-dry the product. This procedure produced fine, free-flowing particulate products at room temperature. All of these, however, partially fused during the thermal cyclodehydration procedure (described later). All products isolated were thus found to be crude agglomerates with very low surface areas, less than about 1 m^2/g.

To determine whether the agglomeration was caused by retained NMP (considered unlikely due to polymer yields that were consistent with the theoretical values), some of DADS/PMDA Polymer 10 was dissolved in NMP. Two 1.0-gram samples of Product 10 were dissolved in about 13.3 grams of NMP (~15 percent solids). The polymer solutions were then precipitated with acetone and water at room tem-

perature, to light, flocculate precipitates. After thorough washing, with acetone and water, respectively, and freeze-drying from water, the products were both still very light, fine powders, weighing 0.90 and 0.95 grams, respectively. The weights indicated no NMP was retained. Upon cyclodehydration, these products remained powders, although they did appear to densify some in the process. The surface areas of the products were low, 2 m^2/g and 4 m^2/g, respectively (described later).

Repetition of this process, with 10 percent urea added to the NMP solutions, resulted in similarly good appearance of powders with good improvement in the measured surface areas of the acetone-precipitated product (14 m^2/g). The surface area of the water-precipitated product was not measured because of an experimental problem.

Polymer Yield

The THF yield data are listed in Table 2. The substantially lower yield of DADS Polymer No. 1 is attributed to the fact that the PMDA addition to the reaction zone was carried out at 32-40 C and the reaction mixture remained a clear, red-orange solution until the temperature was raised to 45-46 C over a period of one-half hour. Copious precipitation then occurred and the product was immediately recovered. However, the reaction probably did not go to completion. In the subsequent DADS/PMDA polymerizations (2, 3 and 10) the PMDA was added at 40-45 C. Most of the PMDA was thus added before the precipitation started. The reaction temperature was then raised to 60 C and held there while stirring overnight. However, in Experiment 3, the temperature inadvertently rose to ~65 C. This appeared to drive the reactions substantially to completion. The powders were suction-filtered on a Teflon-coated glass fiber filter and washed with chloroform.

The polymer yields observed for Experiments 2, 3, 10 and 11 were all very close to 100 percent prior to Soxhlet extraction with diethyl ether. The recorded yields are, however, for the ether extracted (Soxhlet, 16 hours), vacuum dried, yellow powder products. The higher yield and molecular weight of Product 3 (relative to Product 2) are attributed to the slightly higher reaction temperature (65 C) while the Products 10 and 11 results are attributed to the higher purity DADS and PMDA monomers used in those experiments. The polyamide-acid products are, at this point, ready for cyclodehydration to the desired polyimides.

The DADS/PMDA polyamide-acids (Polymers 12, 13 and 14) made in NMP (Table 3) were all obtained in nearly theoretical yields. However, the molecular weights of the products were similar to DADS/PMDA Products 3, 10 and 11, rather than substantially greater as had been anticipated. The reason is unknown. However, it seems likely that it is either due to impurities or is an inherent characteristic of this monomer pair. Since the monomers and the NMP solvent were carefully purified and dried, it seems likely that the known relatively low reactivity of this monomer pair is the main source of this result. However, impurity effects are magnified in solution and may also be important.

The DADM/PMDA polymerizations were carried out at 0 C, using an ice/water bath to cool the reaction mixture. This procedure was used by the prior workers(1) because DADM is a much more reactive diamine than DADS, resulting in an exothermic reaction with PMDA. After all the PMDA was added at 0 C, the yellow solution was rapidly heated to 60-62 C for 1 hour, resulting in copious precipitation of an orange powder. Then the reaction was stopped by cooling to room temperature and the polymer filtered as before. The product was dried and then Soxhlet extracted with diethyl ether overnight. The higher molecular weights of Products 5 and 6, compared to the other Products 1 through 14, are attributed to the higher purity PMDA (thrice sublimed, estimated purity, 99.8 percent, cf. p. 14).

The DCPDA/PMDA Reactions 7 and 8 were carried out in a similar manner to the DADS reactions. However, after heating overnight at 60-65 C, the reaction mixtures remained clear, reddish-brown, solutions, with no precipitate. Even when cooled to room temperature, no precipitation occurred. Only when chloroform (HPLC grade) was added did polymer precipitate. In Reactions 7 and 8, a 3/1 volume ratio of chloroform (e.g., 1800-ml to 600-ml reaction mixture) was added, producing 3.02 and 5.22 g (9.9 and 11.9 percent yields) of yellow powders, 7a and 8a, after diethyl ether (Soxhlet) extraction. The additional product (7b and 8b) was recovered by drying the filtrates and Soxhlet extracting with diethyl ether. Total yields of ether-insoluble product were thus 94.4 and 92.4 percent for Products 7 and 8.

Experiment 9 was carried out slightly differently. The THF solution of DCPDA was heated to 60 C before the PMDA was added. Otherwise the reaction procedure was the same. However, the higher yield (17.9 percent) and higher molecular weight (M_v = 3000) are attributed to this procedural change. Again, Product 9b was recovered by evaporating the filtrate and Soxhlet extracting the residue with ether. Total product yield (9a + 9b) was 95.4 percent.

It had been intended to prepare polyimides from DADM/PMDA and DCPDA/PMDA by carrying out the reactions in NMP solvent, as was described above for DADS/PMDA. However, very low surface areas were obtained for THF polymerized polymers of these two monomer pairs (see Table 5), and also very poor properties were obtained from the polymerization of DADS/PMDA in NMP (low molecular weights and low surface areas of precipitated products, cf Tables 4 and 5). This resulted in the decision not to carry out these polymerizations since it was almost certain they would be unproductive.

Polymer Solution Viscosity and Molecular Weight

The molecular weights of the polyamide-acids were determined in a good solvent for this precursor polymer form, dimethyl acetamide (DMAC), according to the procedure of the prior workers(1). Distilled, dry DMAC was used and the viscosities were determined on 0.5-gram/dl solutions, at 30.0 + 0.1 C, using pressure equalizing Ubbeholde-type viscometers. The inherent viscosities were calculated from $[\eta] = \ln$ relative η/c. The approximate viscosity molecular weights (M_v) were then calculated from the equation $M_v = 4.42 \times 10^4 [\eta]^{1.28}$. This expression was derived by Sroog for the polyamide-acid based on PMDA and 4,4'-diaminodiphenylether and is only accurate for this particular polymer. This

TABLE 4. THERMOGRAVIMETRIC ANALYSIS OF POLYIMIDES[a]

Polyimide Number	Polyimide Type	Percent Weight Loss			
		300 C	400 C	500 C	600 C
119[b]	DADS/PMDA	8.5	14.8	19.5	30.5
1[c]	"	3.4	7.0	13.0	33.0
2[c]	"	5.6	10.0	11.5	26.5
3[c]	"	5.7	9.0	10.8	25.0
149[b]	DADM/PMDA	2.0	2.3	3.2	30.5
4[c]	"	1.8	2.6	3.2	28.0
5[c]	"	5.0	5.5	6.6	27.5
6[c]	"	3.4	3.9	5.0	29.0
140[b]	DCPDA/PMDA	4.2	6.2	11.0	18.2
7a[c]	"	1.2	2.0	4.5	15.0
8a[c]	"	2.6	4.4	6.8	16.8
9a[c]	"	2.6	4.0	8.8	19.5

(a) All samples ∿10 mg.

(b) Polyimides from prior work.(1)

(c) Polyimides from the present work.

TABLE 5. POLYIMIDES MADE IN THF--PARTICLE SIZES AND SURFACE AREAS

No.	Composition	Particle Size Distribution, Weight Percent, μm			Surface Area, m^2/g, μm		
		>212	<212->105	<105	>212	<212->105	<105
	Tenax®	--	--	--	--	25	--
1	DADS/PMDA	34	27	39	--	--	15[a]
					26[b]	--	26[b]
2	DADS/PMDA	31	39	30	--	--	38
3	DADS/PMDA	23	39	38	34	50	--
4	DADM/PMDA	5	10	85	--	--	2.4
5	DADM/PMDA	4	8	88	--	--	4.6
6	DADM/PMDA	3	6	91	--	--	2.1
7	DCPDA/PMDA	59	38	3	--	0.5	--
8	DCPDA/PMDA	33	40	27	--	0.1	--
9a	DCPDA/PMDA	49	34	18	--	21	--
9b	DCPDA/PMDA	67	20	13	--	4.1[c]	--
10	DADS/PMDA	42	26	32	32	--	--
11	DADS/PMDA[d]	40	30	30	24	--	--

(a) Cyclodehydration to 300 C.

(b) Cyclodehydration to 230 C.

(c) Product 9b (cf Table 2, footnote g).

(d) N-phenyl imide end groups (cf Table 2, footnote h).

is because the viscosity is a function of chain stiffness, as well as chain length, and the stiffness or flexibility is expected to differ, depending on the diamine reacted with PMDA. However, to a first approximation, the M_v values reflect the actual molecular weights of the polyamide-acids, and the values are accurate on a relative basis for a given series of products, such as DADS/PMDA polyamide-acids.

As stated earlier, there are specific reasons why the yields and molecular weights of the later products in a given series are higher. The higher values for DADS/PMDA Polymer No. 3 and for DCPDA/PMDA Polymer No. 9 are attributed to the higher final reaction temperatures used. The increases for DADM/PMDA Polymer Nos. 5 and 6, compared to No. 4, are because of higher purity PMDA. Finally, the higher values for DADS/PMDA Polymer Nos. 10 and 11 are due to the use of higher purity DADS and PMDA in this reaction than was used in earlier Reactions 1-3. The reason the molecular weights of DADS/PMDA Polyamide-Acids 12-14 are no higher than Polymers 10 and 11 is probably due to the inherent low reactivity of this monomer pair. However, the action of impurities (amines or water) cannot be entirely ruled out, since these can be difficult to remove and their presence, especially water, is known to have a very strong impact on polymer molecular weight. Water, present in small amounts, is more likely to reduce molecular weight in the solution mode both because it becomes much more effective in competing with aromatic amine groups for the PMDA and because in solution it can cause a rapid cleavage (hydrolysis) of the polymer chain, thus lowering the achievable molecular weight.

CYCLODEHYDRATION TO POLYIMIDES

The polyamide-acid powders were prepared for cyclodehydration by manually grinding into small pieces with a mortar and pestle, and screening through a 35-mesh sieve. The 35-mesh powders were put in a round-bottom, one-neck, Pyrex flask (usually 7-10 grams in a 250-ml flask) which was then attached to a rotary evaporator. The powder was dehydrated by heating from ambient to 230 C, then holding at 230 C for about 2 hours, at a rotation rate of 30 rpm, under a vacuum of about 7 Pa. Heating was accomplished with a silicone oil bath, with the rotating flask submerged about one-third in the oil. The weight of the powder was checked at approximately 15-minute intervals after reaching 230 C. It thus was determined that the powders reached a constant weight, corresponding to a nearly theoretical yield of water, in less than 2 hours at 230 C.

POLYIMIDE CHARACTERIZATION

Thermogravimetric Analysis

Polyimide powder Products 1-9 (200-500 μm fraction) were subjected to thermogravimetric analysis (see Table 4 and Figures 1-9). About 10 mg samples were used in the TGA experiments, which were done using a Cahn TGA Apparatus at a

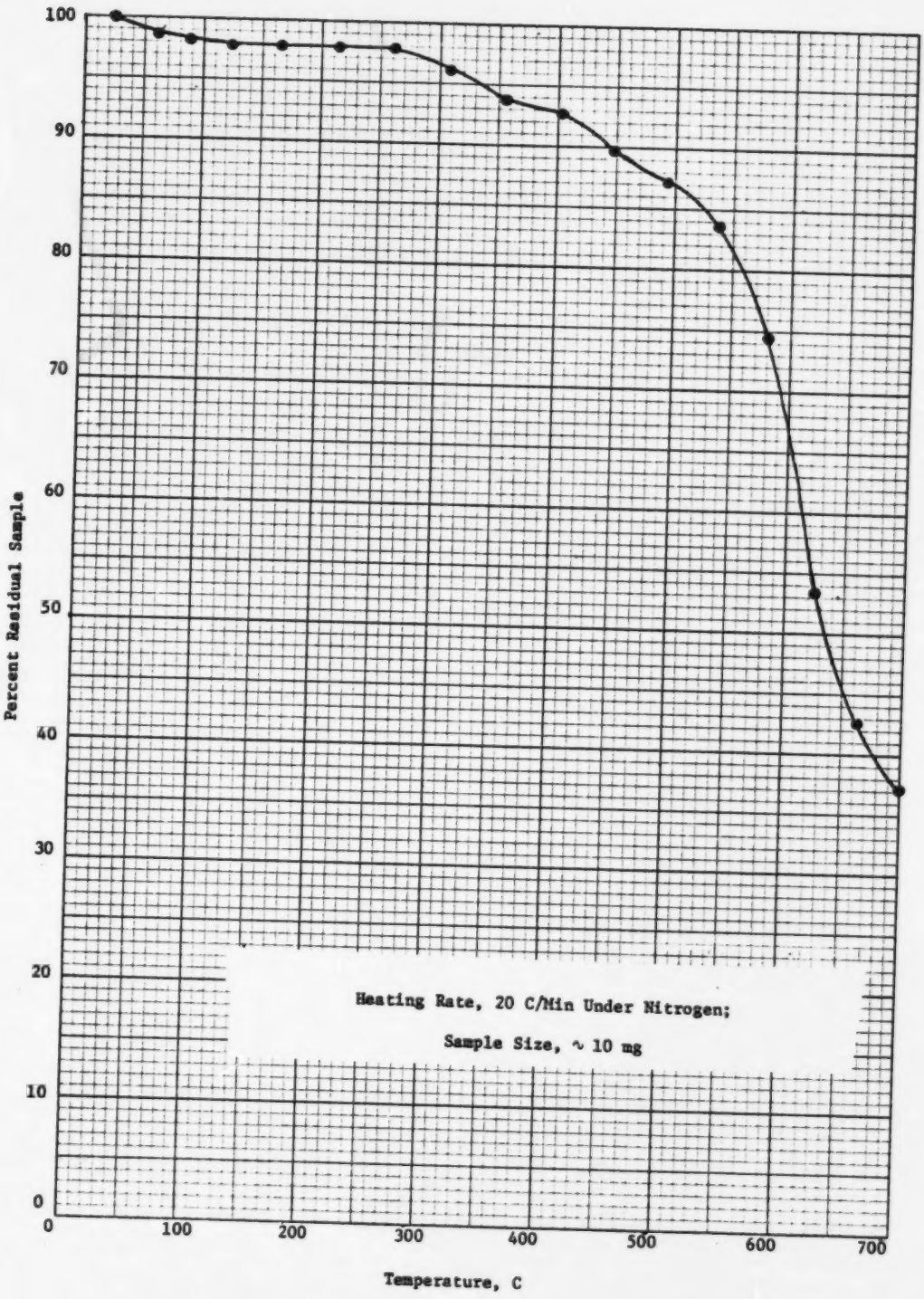

FIGURE 1. THERMOGRAM OF DADS/PMDA POLYIMIDE -- POLYMER NO. 1

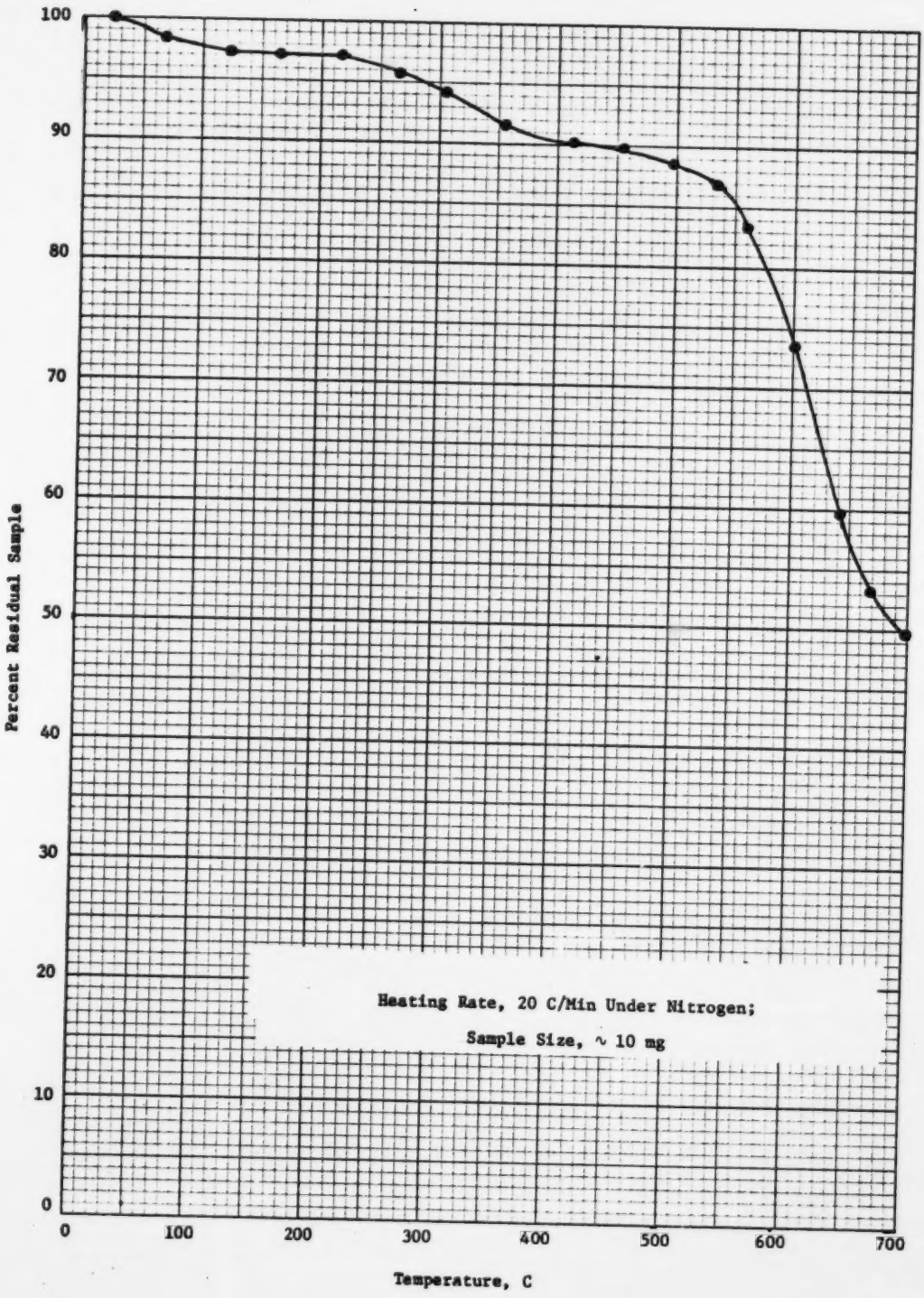

FIGURE 2. THERMOGRAM OF DADS/PMDA POLYIMIDE -- POLYMER NO. 2

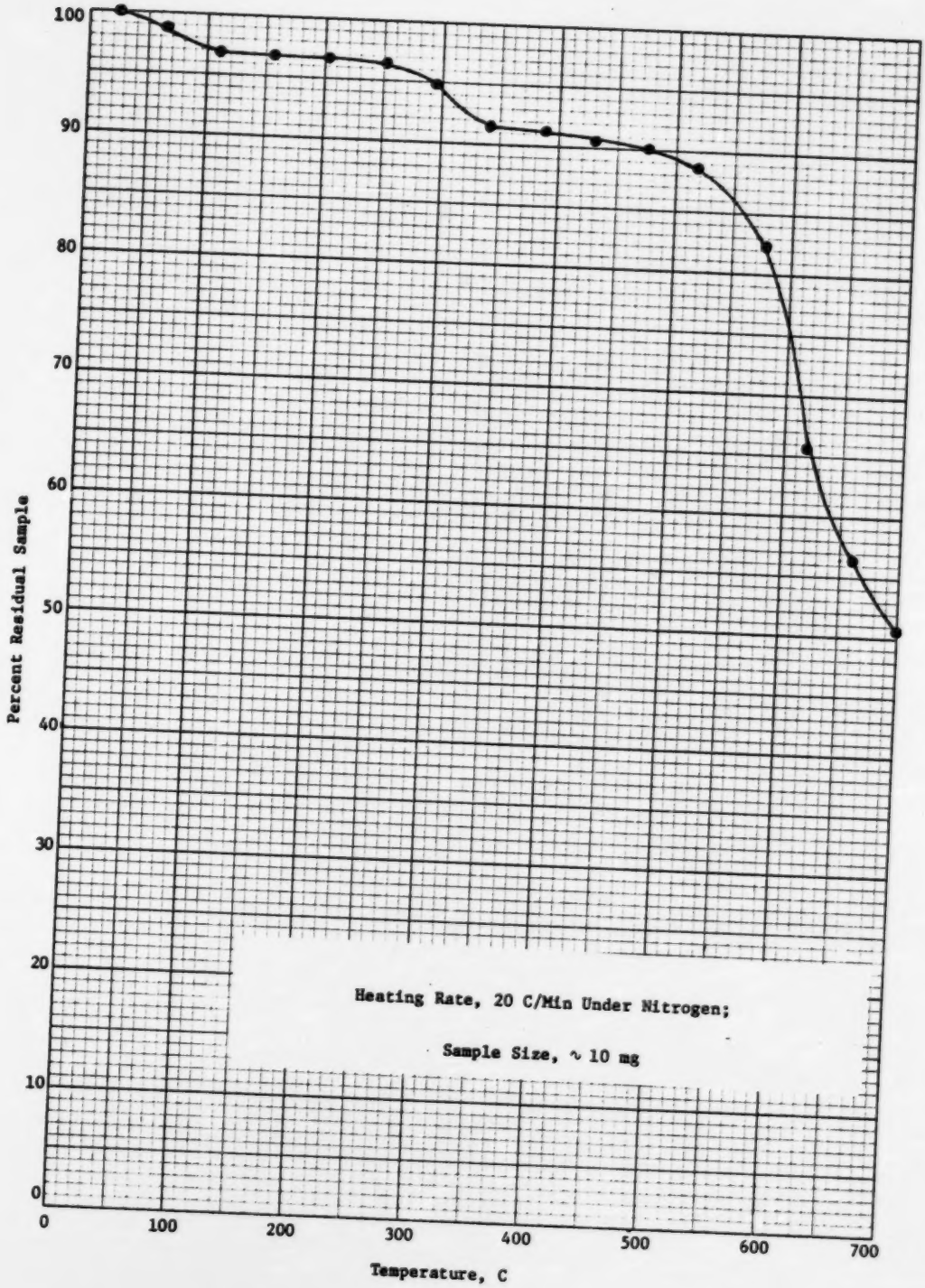

FIGURE 3. THERMOGRAM OF DADS/PMDA POLYIMIDE -- POLYMER NO. 3

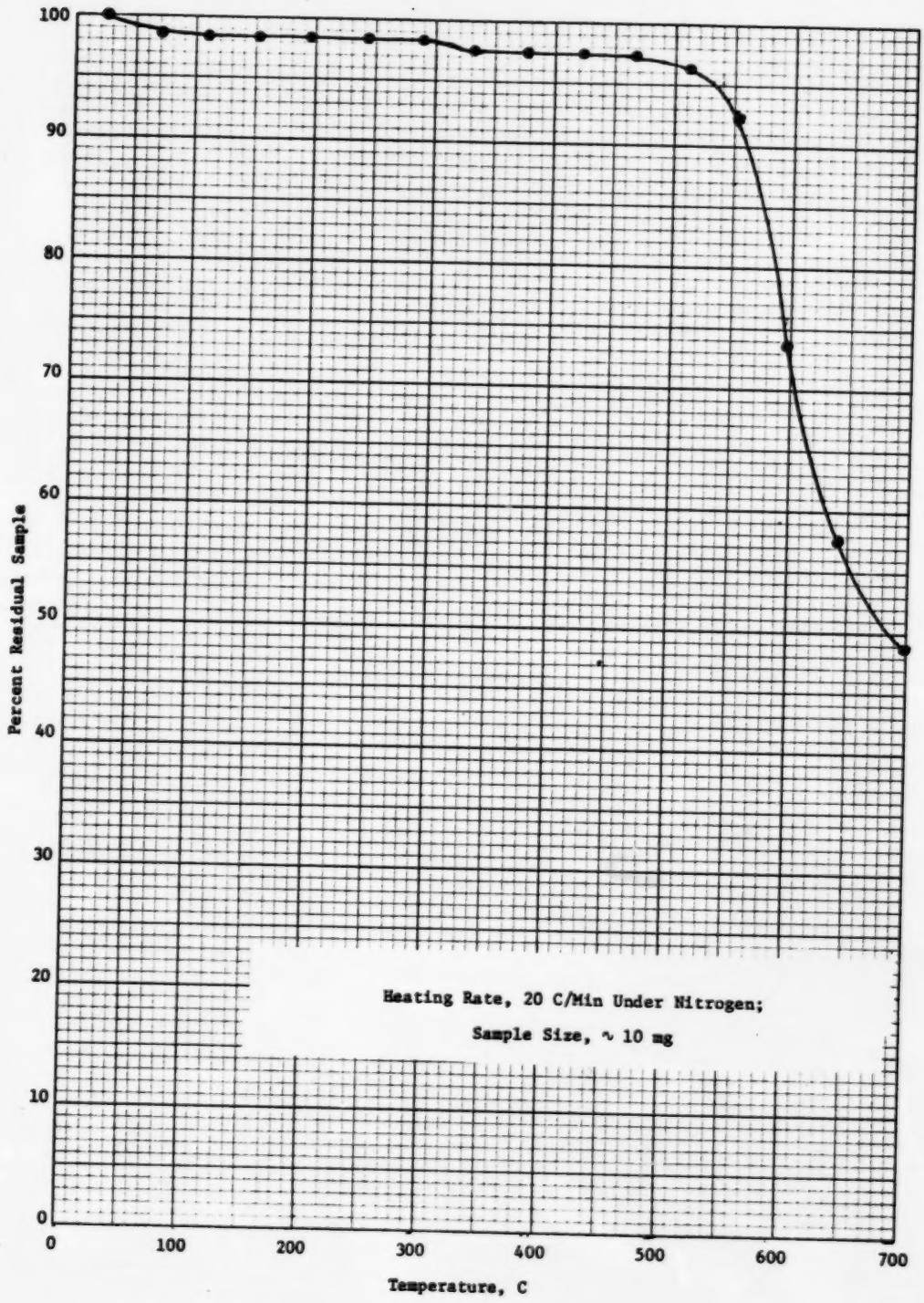

FIGURE 4. THERMOGRAM OF DADM/PMDA POLYIMIDE -- POLYMER NO. 4

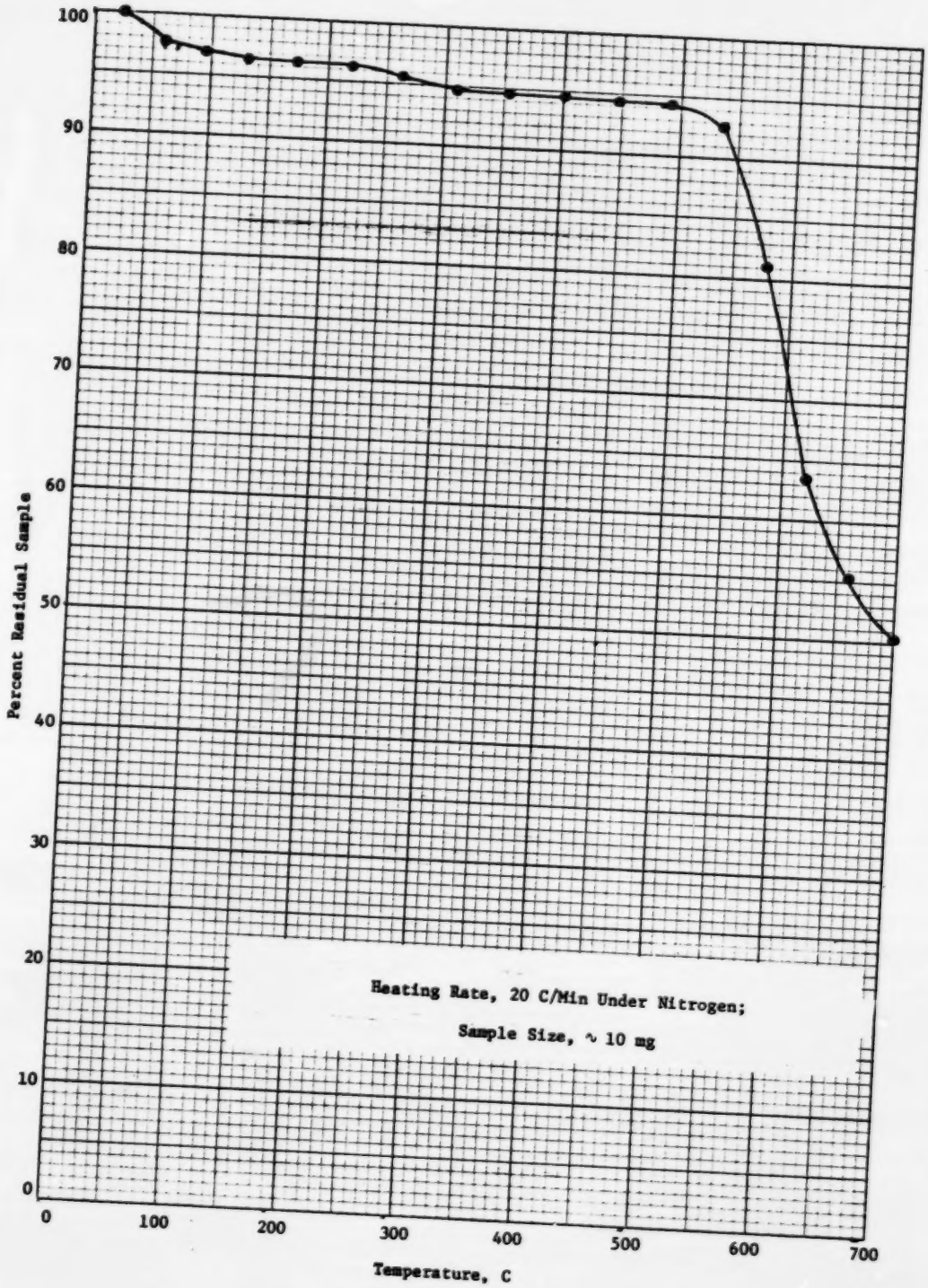

FIGURE 5. THERMOGRAM OF DADM/PMDA POLYIMIDE -- POLYMER NO. 5

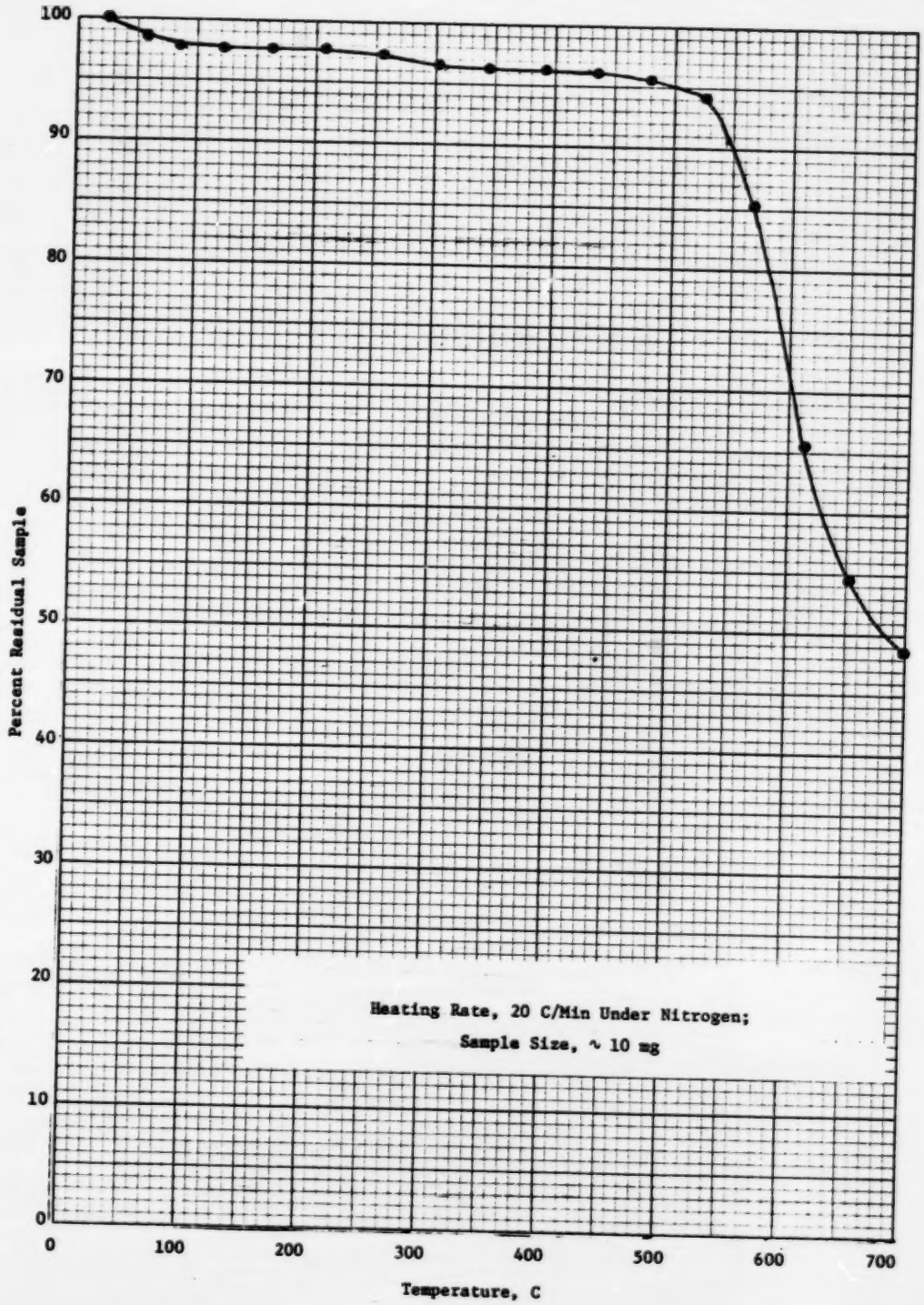

FIGURE 6. THERMOGRAM OF DADM/PMDA POLYIMIDE — POLYMER NO. 6

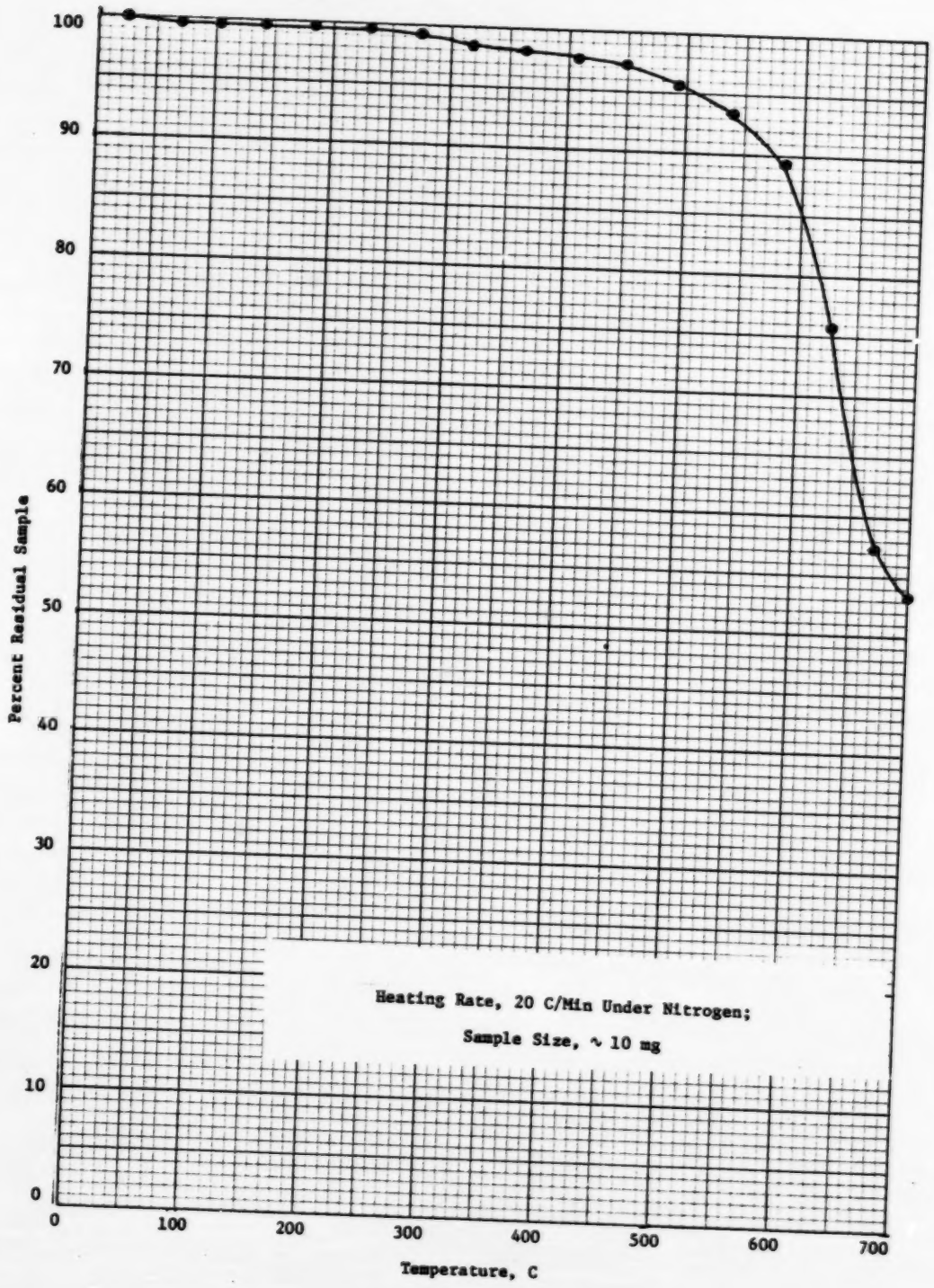

FIGURE 7. THERMOGRAM OF DCPDA/PMDA POLYIMIDE -- POLYMER NO. 7

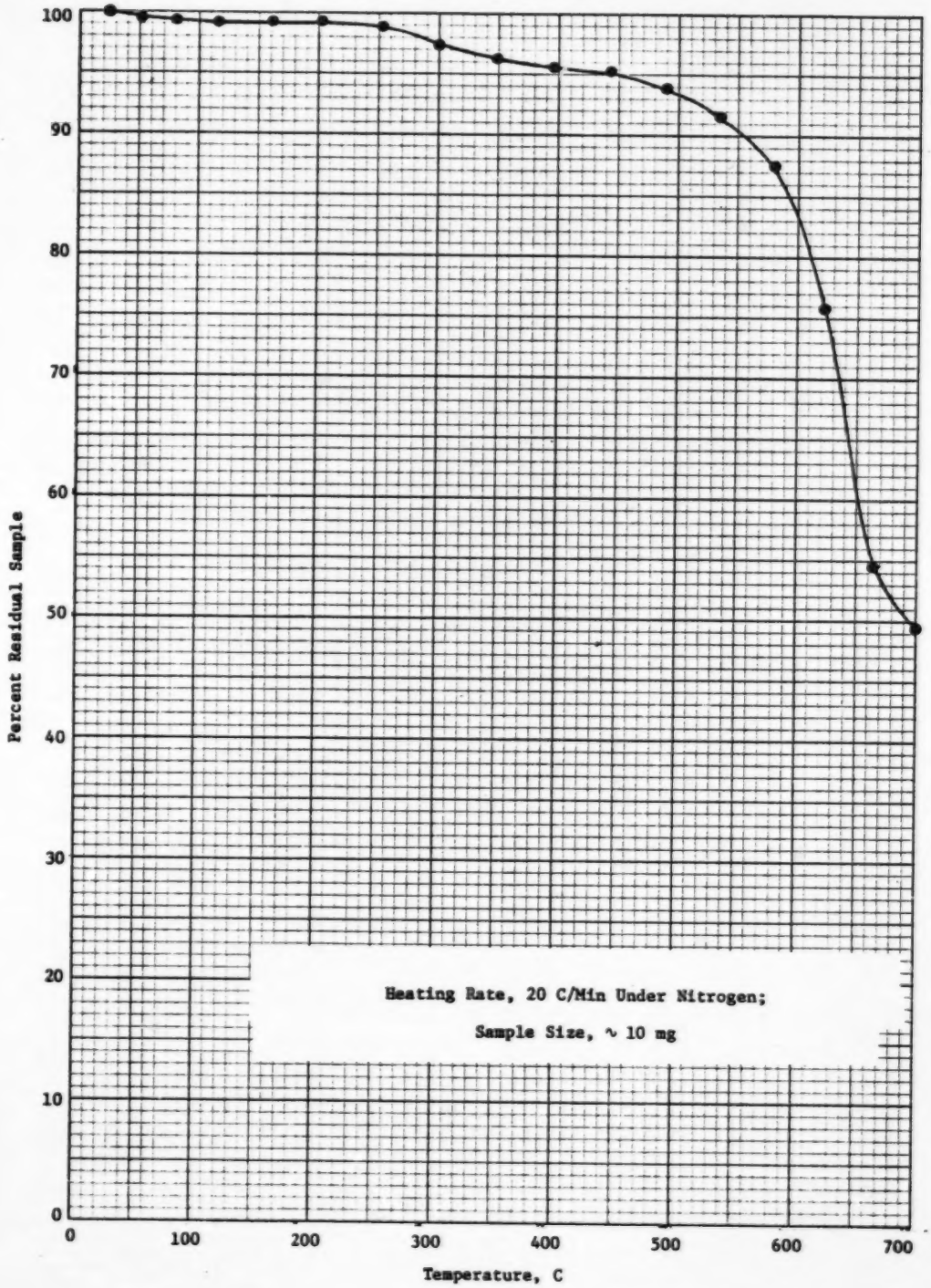

FIGURE 8. THERMOGRAM OF DCPDA/PMDA POLYIMIDE -- POLYMER NO. 8

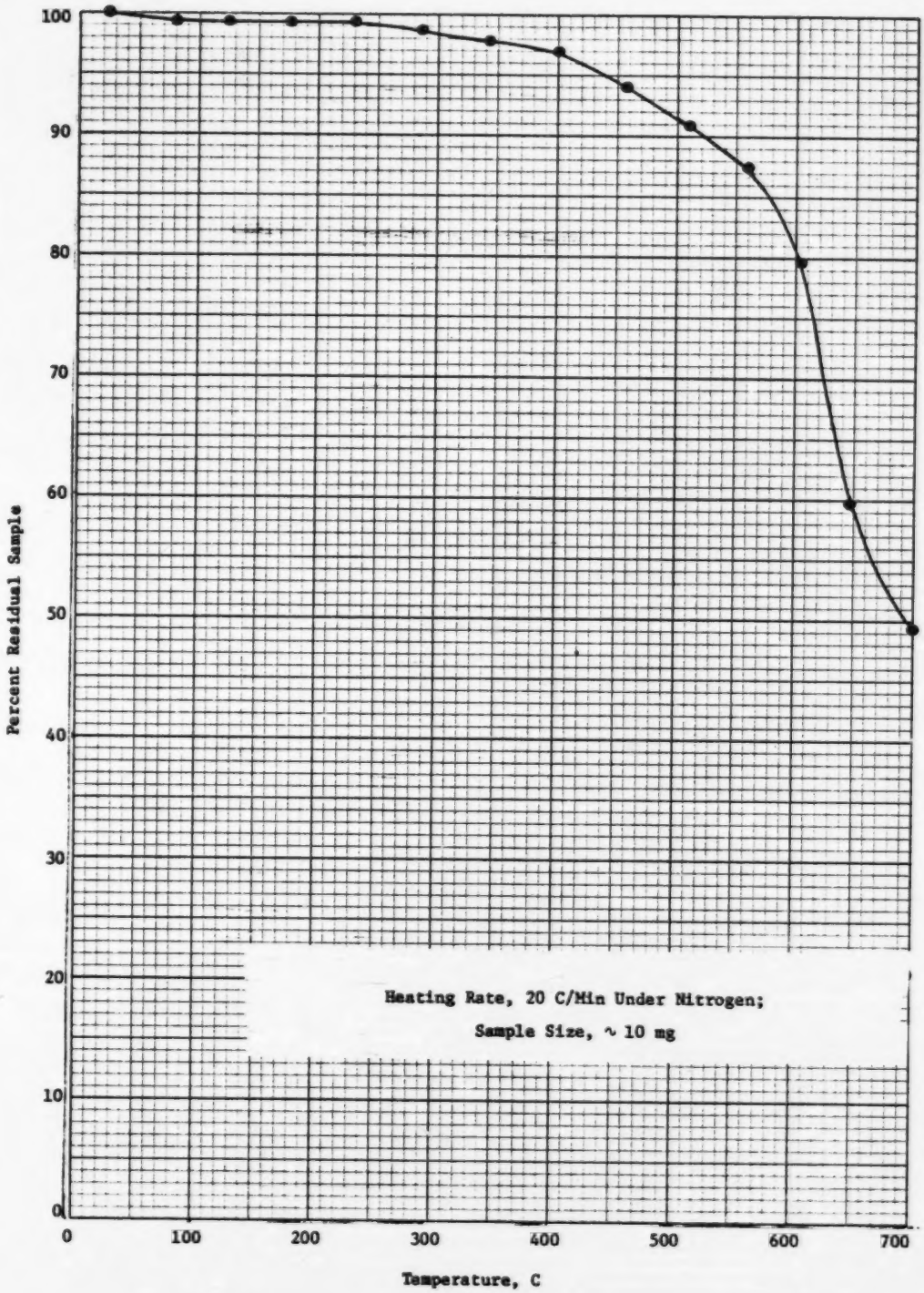

FIGURE 9. THERMOGRAM OF DCPDA/PMDA POLYIMIDE -- POLYMER NO. 9

programmed rate of 20 C/min, under (nitrogen) as in the prior work.(1) However, in the prior work, the samples were first taken to 300 C, held 5 minutes, then cooled to 50 C and the instrument reset to a sample weight of 100 percent. Then the TGA weight loss curve was recorded to 700 C at 20 C/min. In the present work the samples were programmed to 700 C at 20 C/min, with no preheating. This approach was based on the assumption that the following features of the TGA curves are meaningful and should be obtained in an undistorted form. These are (a) the earliest weightloss and its magnitude, (b) the presence of plateaus or relatively stable temperature ranges, and (c) changes in slope, especially in the early part of the heating cycle. These TGA features, which vary slightly for each polyimide type, can ultimately be related to polyimide stability in the 20-300 C range and to the physical or chemical processes leading to the observed weight losses and weight loss rates.

The TGA weight losses observed in prior work(1), including the sum of the weight loss occurring during the 300 C conditioning period plus the additional losses recorded during the actual TGA run (cumulative total weight loss), are recorded for representative DADS/PMDA (119); DADM/PMDA (149); and DCPDA/PMDA (140) polyimides at 300, 400, 500, and 600 C in Table 4. Samples 119, 199 and 140 are sample numbers in reference 1. These losses can be compared to the TGA weight losses recorded at these respective temperatures for Polyimides 1-9 in the present work. It can be seen that the weight losses for the DADS and DCPDA polyimides were higher at the lower temperatures (300-500 C) in the prior work but were quite similar to the losses in the present work at 600 C.

All the polyimides from the present work show similar, small weight losses (1.2-2.7 weight percent) between 20 C and ~100 C followed by a plateau region to ~250 C. These initial weight losses are almost certainly a combination of physical losses of adsorbed water or solvents which were not completely removed during the cyclodehydration of the relatively large quantities of polyamide-acid, in the polyimide forming step, or were in part readsorbed during sample handling. In the TGA procedure much lower pressures are achieved using a very small, high exposed surface, sample than those achieved during the cyclodehydration procedure. Hence, the removal of these volatile species is highly efficient and quantitative.

At about 250 C a second region of weight loss starts with a relatively rapid weight loss of several weight percent loss occurring between ~250-350 C, followed by a decrease in rate to about 500 C. However, the rate of weight loss never becomes completely level between 250 and 500 C. The nature of this weight loss is unknown, but it probably represents the onset of a slow chemical degradation of the polyimide. It could also represent slow release of more strongly physically adsorbed species. Above 500 C all of the polyimides begin to degrade more rapidly.

It is concluded that all the polyimides are stable to ~250 C and are probably usable for very long times up to this temperature, barring chemical attack by some very aggressive compounds. However, above ~250 C the useful lifetimes of the polyimides may be more limited and some development of volatile background may occur. It may be necessary at some time to determine the nature of the volatile products in this region to determine whether in fact they are simply physically adsorbed or are thermally induced degradation products. If they are adsorbed species, some program of column conditioning between 250 and 300 C, under

inert gas should provide a very stable, low elution background, sorbent powder. If the volatiles are chemical degradation products, identification of these products may elucidate the degradation mechanism and allow preparation of a more stable polyimide.

Particle Size

The polyimide powders obtained after the cyclodehydration step were separated into three fractions by following standard procedures for powder classification. Three sieves (212, 149 and 105-μm openings) were used in vertical, stacked combination on an automatic vibrator apparatus. Eight to ten grams of the polyimide powders were placed on the top, coarsest sieve (212 μm), and the stack was vibrated for five to ten minutes until the powder weights at each level were constant ($\sim$ 5-10 minutes). Four powder particle sizes were obtained (>212, <212- 149, <149->105, and <105 μm). The 212-149 and 149-105 μm fractions were combined to give the three fractions shown in Table 5.

The most readily handled powder size for use in packing sorbent columns is 200-500 μm. Thus it is necessary to have the maximum amount of the fraction 212 μm. This fraction is highest for DCPDA/PMDA Polyimide Product Nos. 7-9, ranging from 33 to 67 percent of the total. It is second highest for the most promising experimental polyimide sorbents, DADS/PMDA Polyimide Nos. 1-3 and 10 and 11, ranging from 23-42 percent of the total. Surprisingly, it is quite low for the DADM/PMDA Polyimide Nos. 4-6, ranging from 3-5 percent. These latter polyimides are mostly very fine powders (<105 μm), which are difficult to handle because of severe dusting and static electricity problems.

It is felt that the particle size ranges obtained are controllable to some extent by variations in reaction procedure such as rate of PMDA addition to the reaction zone, reaction temperature/time profile, and procedures in handling during work-up of the products, especially during the preliminary sizing before the cyclodegradation step. This aspect of the polyimide synthesis is beyond the scope of this project but will need to be addressed in the future.

These polyimides are rather brittle and weak and are therefore easily mechanically broken into smaller particles. One of the primary factors affecting their physical weakness is the low molecular weights. As a rule of thumb, polymers of this class will begin to develop toughness and resistance to facile breakage at molecular weights of about 10,000. This is one reason for attempting to prepare the most promising polyimides at higher molecular weight levels than have so far been obtained.

BET Surface Area

The surface areas of the polyimide powders were measured by the BET nitrogen adsorption method using a dynamic gas adsorption unit. Nitrogen is adsorbed as a function of temperature at reduced pressures. The method is more accurate than mercury porosimetry, especially the smaller pore sizes associated with the higher surface areas (≥ 25 m^2/g) of interest in this work.

The surface areas of selected powder fractions were measured and the data recorded in Table 5. Tenax GC was measured for comparison (25 m^2/g). This value is in agreement with the data provided by the supplier of this product and with published values. The surface areas of the DADS/PMDA polyimides were the highest, ranging from 15-50 m^2/g. All of the values were greater than the value for Tenax GC.

The sample measuring 15 m^2/g was inadvertently heated to 300 C during the cyclodehydration step. This temperature may be above the glass transition temperature (Tg) for this polyimide, which at the relatively low molecular weight of 3,600 could result in some collapse or reduction of the micropore structure. This would reduce surface area. This is another reason why higher molecular weights would be very desirable. Softening behavior (Tg) increases with molecular weight for this type of polymer up to molecular weights in the range of 10,000 to 20,000.

A second portion of Product 1 was carefully cyclodehydrated at an upper temperature of 230 C and two particle size fractions of this powder (>212 μm and 105 μm) both gave results of 26 m^2/g. This agreement in surface area between particle size fractions was expected. Consequently, it was surprising to obtain a surface area difference between two particle size powder fractions of DADS Product 3 (>212 μ, 34 m^2/g; <212->105 μm, 50 m^2/g). On the basis of data currently available[5], it is believed that these results may be within experimental error of + 50 percent at these higher surface area levels. Replicate BET measurements of various particle fractions would be needed to establish the experimental precision for these products. However, the additional work was beyond the scope of this study.

The remaining surface area results for the DADS polyimides made in THF are quite consistent for different particle sizes and different products ranging from 3,400 to 7,000 in molecular weight. The average value is 34 m^2/g. This is 40 percent greater than the value measured for Tenax GC. However, the difference between 25 and 34 m^2/g is not at present statistically significant.

Interestingly, this is consistent with the bulk density values of Tenax GC (0.166 g/mL) and the 10 percent lower average value for DADS products 1, 2, and 10 (0.153 g/cc) found on a related project.[5] The low bulk densities arise either from particles <0.01 μm in diameter, or from extensive micropore structure of this magnitude in larger particles. The physical evidence indicates that a microporous structure of some type is the source of the high surface areas. To a first approximation the 10 percent lower bulk densities of the DADS polyimides are a function of the high porosity/surface areas.

On the other hand, the surface areas of DADS polyimides produced by NMP polymerization were <1 m^2/g regardless of the method of precipitation due to fusion of the primary particles during cyclodehydration. However, when Product 10, made in THF, was dissolved in NMP and precipitated by either acetone or water, fine particle precipitates were obtained which could be washed with water to apparently remove all NMP. These were then slurried in water and freeze-dried to yield fine, dry powders. These powders survived the thermocyclodenydration step without fusion. Surface areas as high as 14 m^2/g were obtained if ten percent by weight of urea, based on polyamide-acid, were added to the solution

before precipitation with acetone. It appears likely that further work will produce higher surface area products.

The bulk density of DCPDA/PMDA Product 9a (0.587 g/mL) is high relative to the THF DADS products. Yet the surface area of 9a was found to be 21 m^2/g. This is an anomalous result in view of the above described relationship between bulk density and surface area. However, the other DCPDA products have low surface areas (0.1-4.1 m^2/g) that are in line with the higher bulk densities. Furthermore, the sorption characteristics of Product 9a are very poor, as discussed below, relative to DADS polyimides, in spite of the measured high surface area. It is apparent that the nature of the porosity/surface area in 9a is quite different from that of the THF DADS polyimides. However, the substantially higher surface area of DCPDA Product 9a does indicate that some aspect of the reaction procedure used to prepare that product has a major, and potentially useful, effect on the surface area obtained. The known differences in the preparation of the initial Polyamide-Acid Product No. 9 (cf page 23) were that the PMDA addition step was done at 60 C and the resultant polymer solution was precipitated with a slightly larger amount of chloroform. The higher molecular weight, and the possibly related higher surface area, must be functions of one or both these procedural variations.

The surface areas of DADM/PMDA polyimides (samples numbers 4 through 6) range between 2.1 and 4.6 m^2/g. These are consistent values which are an order of magnitude lower than the surface areas of the DADS polyimides and again indicate that unfavorable sorption properties relative to Tenax GC, or the DADS polyimides are to be expected.

It is concluded on the basis of the BET surface areas that the DADS polyimides made in THF are equivalent or possibly superior to Tenax GC and may be expected to have good potential as sorbents. On the other hand, the DADM and DCPDA polyimides have generally substantially lower surface areas. Consequently, it is probable that they will not have useful sorbent properties.

Sorption Characteristics

The study of the adsorption/desorption characteristics of candidate resins was carried out on a separate program.(5) The samples of DADS/PMDA resin prepared in the present work were studied and showed surprisingly good capacity for adsorption of benzene at 510 ppbv in nitrogen. Figure 10 demonstrates that, although the surface areas of the DADS/PMDA resins were found to be roughly equivalent to that of Tenax GC, they show substantially greater sorption capacity presumably because of a greater development of micropore structure. On the other hand, the more gradual rise of the breakthrough curves indicates poor sorption kinetics since breakthrough of vapor begins well before the saturation capacity of the resin is reached. This signifies lack of adequate large-diameter, "conduit", porosity in these laboratory preparations. The control and development of polyimide structure is a logical next step in the development of these interesting candidates. As was described earlier, this was attempted by the preparation of the polymers in a true solvent (N-methyl-pyrrolidone) to obtain higher molecular weight products. The precipitation of the polyamide-acids from solution by carefully controlled procedures was expected to provide control over

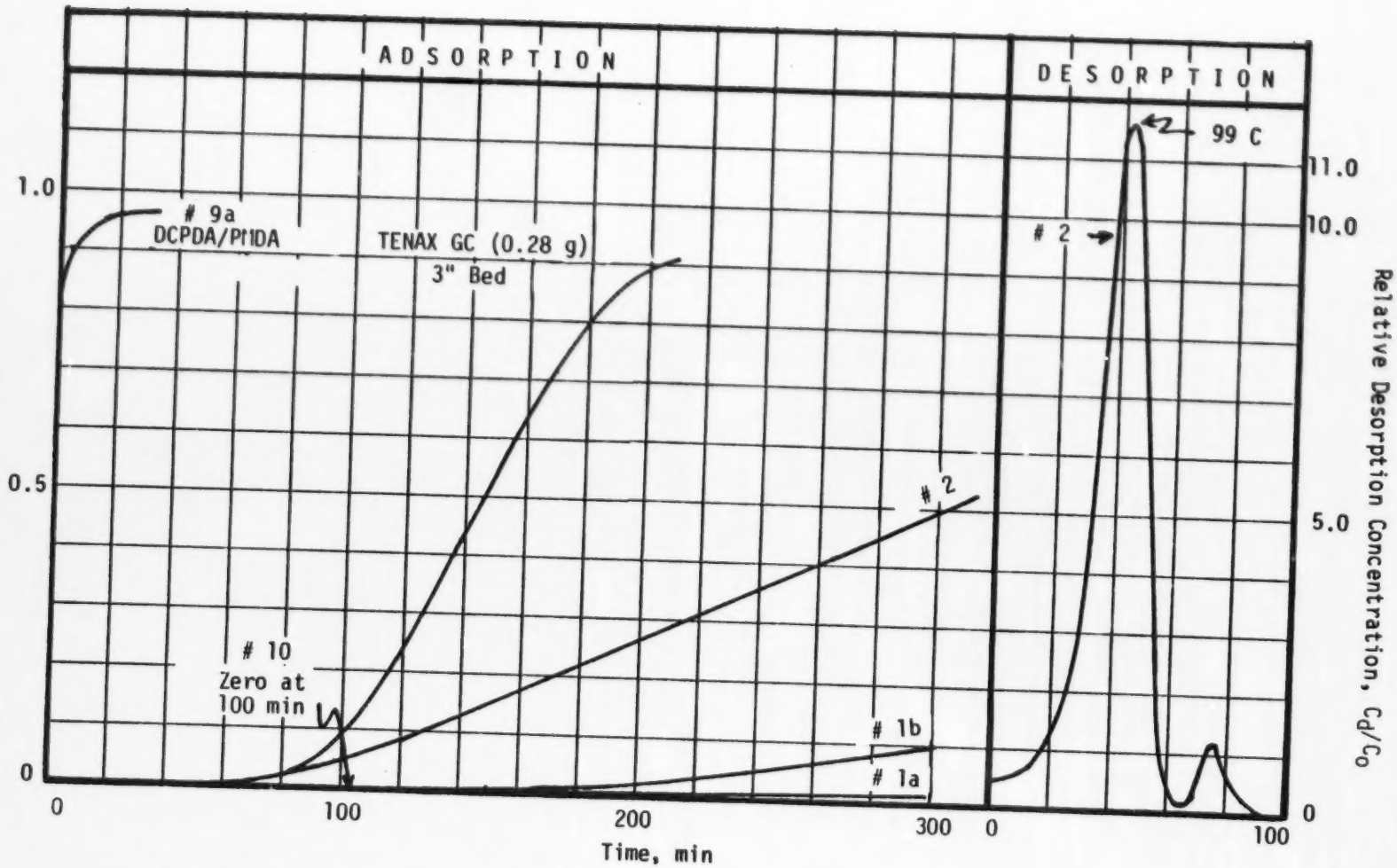

FIGURE 10. VAPOR BREAKTHROUGH CHARACTERISTICS FOR SEVERAL CANDIDATE RESINS COMPARED TO TENAX GC

(Except as shown, all sample numbers refer to 1-1/4 inch Bed Lengths of DADS/PMDA Resin. For comparison purposes, the Desorption Concentrations, C_d, are shown relative to the Inlet Concentration, C_o, used during adsorption.)

the microporosity of the precipitate, but this approach has so far been unsuccessful.

Polyimide No. 9a, representing the DCPDA/PMDA resins, showed very poor breakthrough character(5) in spite of its relatively high surface area (21 m^2/g).

The desorption character of the DADS/PMDA resins is illustrated in Figure 10 by the curve for Sample No. 2. Typically the desorption curves represent 98-103 percent recovery of benzene adsorbed with a desorption peak under this temerature profile at near 100 C. Polyimide Nos. 4-8 (DADM and DCPDA polyimides) and 12-14 (DADS polyimides made in NMP) were not studied for benzene breakthrough characteristics due to their low surface areas.

Scanning electron microscope (SEM, 20,000X magnification) photomicrographs of THF precipitation polymerized DADS Products 1, 2 and 10 are shown in Figures 11, 12, and 13, respectively. Product 11 (not shown) is essentially the same as 10 in appearance, although it has a somewhat lower surface area (24 m^2/g). This difference is probably not significant. DADS Polyimide 1 (Figure 11) shows a distinct microstructure pattern of flat (2-5 μm across), stacked platelets. The platelet thicknesses and the spaces between are on the order of 0.01 μm or less. DADS Polyimide 2 (Figure 12) shows an apparently randomly agglomerated mixture of a rather broad range of irregularly-shaped platelets ($\sim$ 1-0.01 μm diameter) and what appear to be short, poorly defined, rod-like structures ($\sim$ 1-0.1 μm diameter). The photomicrograph of DADS Polyimide 10 (Figure 13) is very similar to that of No. 2 at first glance. However, on closer inspection it is apparent that there is an increase in the rod-like shapes at the expense of the platelets. Again, the rods and platelets appear to be randomly agglomerated with many irregularly shaped voids between the agglomerated pieces. However, the degree of agglomeration appears to be somewhat greater than in DADS/PMDA 2 so that the larger void volume which was thought might occur at higher molecular weight was not obtained.

It is considered likely that the rod-like structures are the first stages of microfibril formation and that the increase in the amount of rods versus platelets on going from DADS-2 to DADS-10 is due to the higher molecular weight of DADS-10. If this is true, the preparation of appreciably higher molecular weight DADS polyimides takes on much greater importance, as well as gaining control over the process by which the polyamide-acids are precipitated from the reaction mixture. It may well be that there is an optimum range of molecular weights which, together with proper control of the precipitation or agglomeration process, will allow well-defined microfibrils to form and agglomerate loosely. It is apparent that maximum useful sorption surface area will be obtained in two ways. The rod or fiber structures should be kept at very small diameters (e.g., <0.1 to 0.01 μm diameter) and they should be loosely agglomerated to obtain the maximum amount of interconnected, or freely available, void volume.

The DADS/PMDA Product 14 sample precipitated with acetone and freeze-dried from water is shown in Figure 14. The fused, low surface area (<1 m^2/g) character is quite evident. The acetone (Figure 15, 2 m^2/g) and water precipitated (Figure 16, 4 m^2/g) samples of Polymer 10, which had been dissolved in NMP show better surface characteristics than the sample of Figure 14, and have small but measurable surface areas. It is of interest to note the spherical

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20,000X

FIGURE 11. SEM PHOTOMICROGRAPH OF
DADS/PMDA POLYIMIDE 1

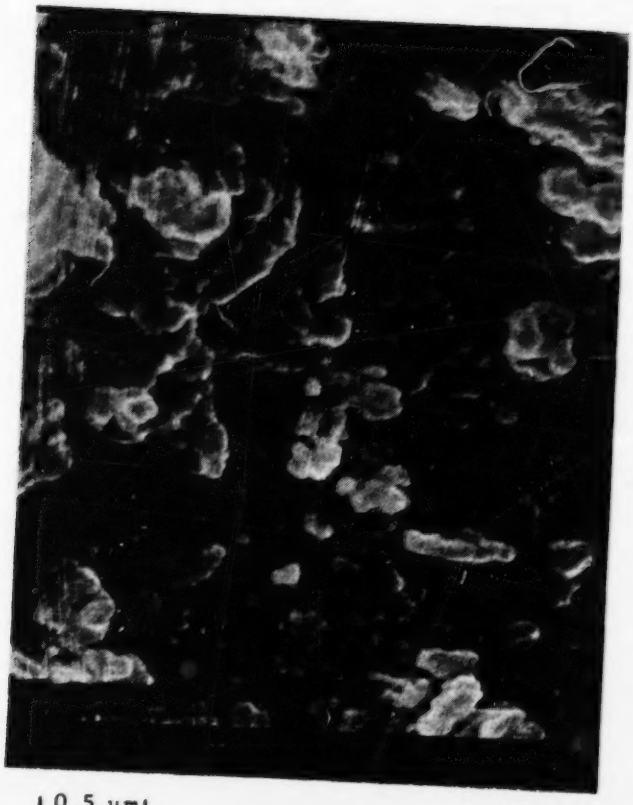

FIGURE 12. SEM PHOTOMICROGRAPH OF DADS/PMDA POLYIMIDE 2

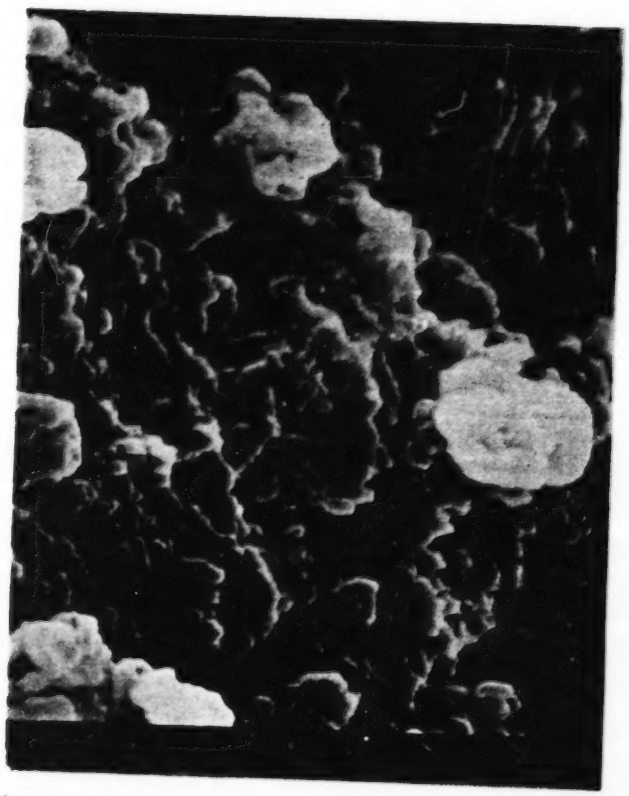

FIGURE 13. SEM PHOTOMICROGRAPH OF DADS/PMDA POLYIMIDE 10

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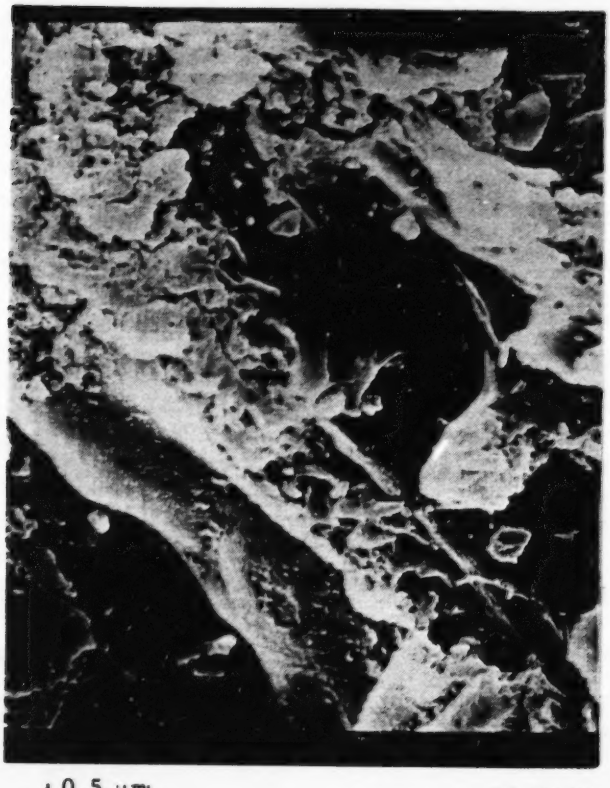


FIGURE 14. SEM PHOTOMICROGRAPH OF DADS/PMDA POLYIMIDE 14, PRECIPITATED WITH ACETONE

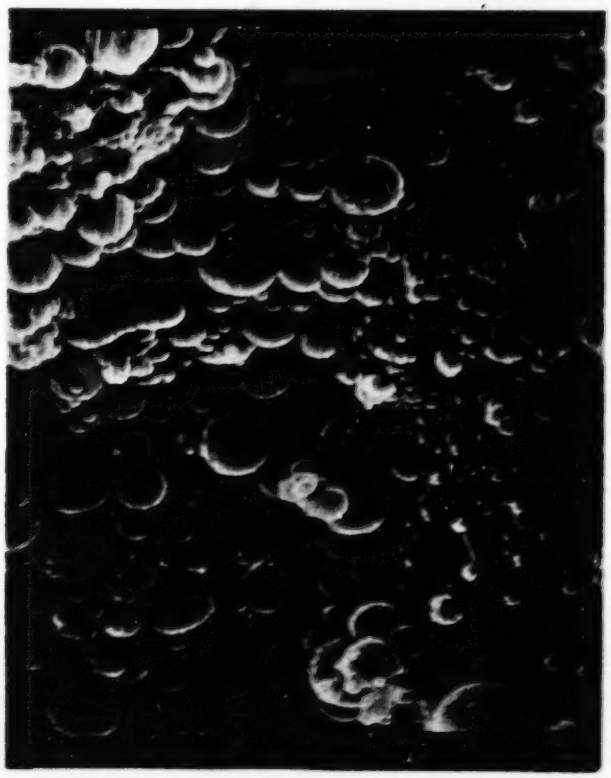
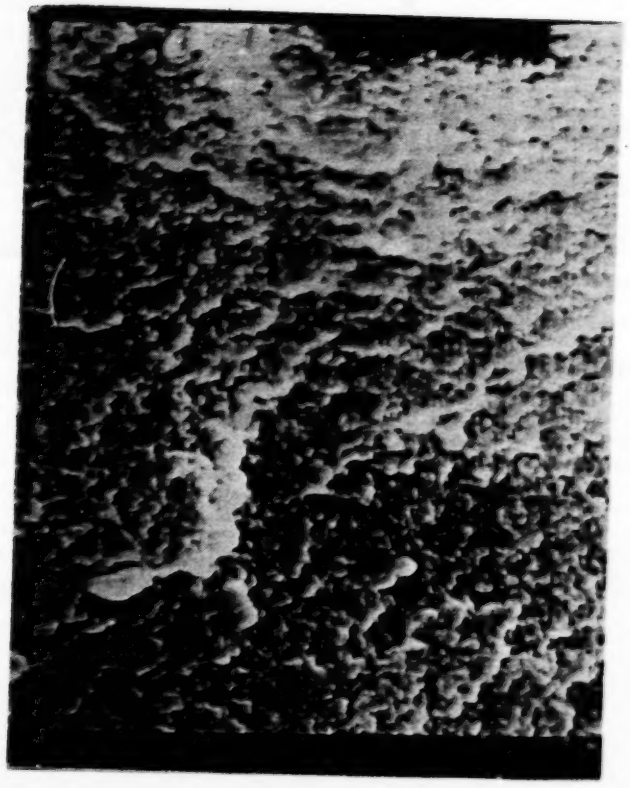


FIGURE 15. SEM PHOTOMICROGRAPH OF DADS/PMDA POLYIMIDE 10, PRECIPITATED WITH ACETONE



0.5 µm

20,000X

FIGURE 16. SEM PHOTOMICROGRAPH OF DADS/PMDA POLYIMIDE 10, PRECIPITATED WITH WATER

particles in the acetone-precipitated product which appear to be solid and non-porous. The water-precipitated sample appears to be partially fused smaller particles, partly microfibrillar, with some remaining porosity.

The two samples of Polymer Product 10 which had been dissolved in NMP, together with 10 percent added urea, then precipitated with either acetone or water are shown in Figures 17 and 18. These appear to have higher porosity than the samples of Figures 15 and 16. This is presumably due to the somewhat higher molecular weight of Product 10. The acetone-precipitated product is entirely spherical and the ($\sim$ 0.1-0.5 μm) spheres appear to be composed of much smaller spheres or particles, not completely fused together. The water-precipitated product also appears to consist of partly agglomerated, very small spheres or particles on the order of 0.01 m. Some of the larger structures have a somewhat fibrillar appearance. The partly agglomerated sections appear to be porous. Apparently the presence of urea in the NMP solution is beneficial, possibly due to its ready removal by water in the work-up process.

REPRODUCIBILITY ASSESSMENT

The properties which can be used to determine the reproducibility of the preparation procedures and polymer products are the following:

- Polymer yields
- Polymer molecular weights
- TGA data
- Particle size distributions
- BET surface areas
- Sorption characteristics.

The polymer yields and molecular weights are not uniform within each set of polymer types produced. However, these results show a definite progression toward higher yields and higher molecular weights, within each of the three sets. This represents improvements in monomer purity and polymer preparation technique in each case. Hence, although later polymerizations in each of the three sets have not "reproduced" the results of the first polymerization of that set, the steady improvement in properties, suggest that the polymerizations are under control. Thus it is projected that the results of Experiments 10, 5 and 6, and 9 are reproducible.

Likewise the TGA weight loss data (Table 2, Figures 1-9) are reasonably consistent within each set. Each polyimide type exhibits a weight loss profile (Figures 1-3, 4-6, 7-9) that is consistent for that polyimide. All the polyimides appear to be very stable to $\sim$ 250 C and the weight losses at higher temperatures, such as 600 C, are quite consistent or reproducible. In particular, the TGA weight losses for the three promising DADS/PMDA polyimides tested are reasonably reproducible with a trend to lower weight losses at 500 C and 600 C for each polymer.

The particle size distributions (Table 4) are quite different for each of the three polyimide sets made in THF but quite reproducible within each set. The particle size distributions possible from precipitation with acetone or water are

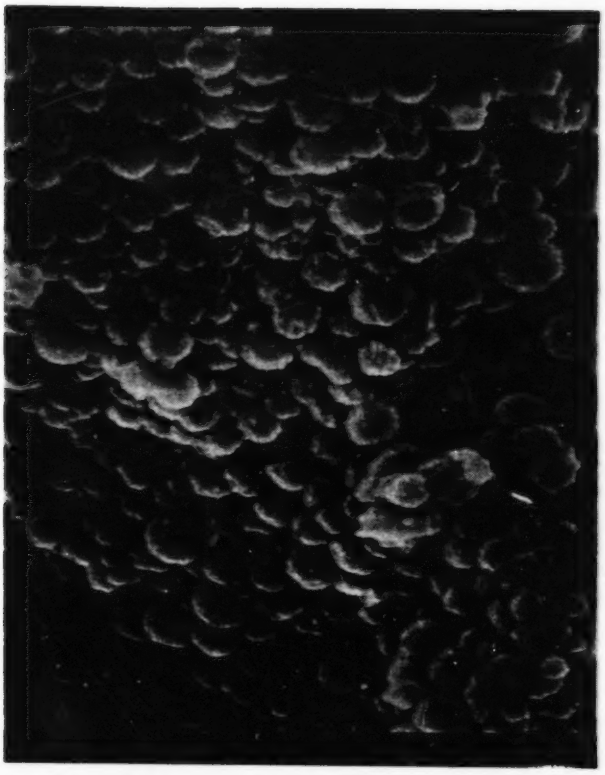


FIGURE 17. SEM PHOTOMICROGRAPH OF DADS/PMDA POLYIMIDE 10, WITH 10 PERCENT UREA, PRECIPITATED WITH ACETONE

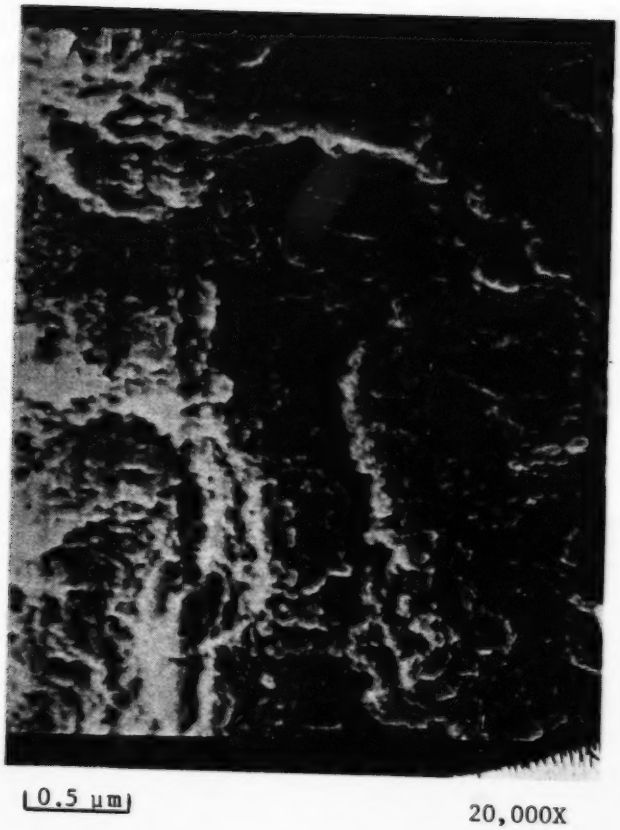


FIGURE 18. SEM PHOTOMICROGRAPH OF DADS/PMDA POLYIMIDE 10, WITH 10 PERCENT UREA, PRECIPITATED WITH WATER

not yet known with certainty, although the amount of product with >212 μ particle size possible appears to be as great or greater than in the products made in THF.

The surface areas (m^2/g) are, with the exception of three data points, very reproducible. The exceptions are the 50 m^2/g area for one DADS polyimide powder fraction (<212-105 μm, polymer No. 3) and the 21 and 4.1 m^2/g data for the same particle size DCPDA Polyimide No. 9 (9a and 9b). It is most encouraging that the surface areas are so reproducible, since this is the most important properties of the polyimides along with sorption characteristics.

The sorption properties have not been sufficiently studied to properly assess their reproducibility. However, the data obtained so far indicate that DADS/PMDA polyimides with obviously similar microstructures and surface areas, such as DADS 2 and 10, exhibit apparently equivalent breakthrough volumes which are superior to Tenax GC. More work needs to be done to assess the kinetics of the sorption desorption process, the sorption capacity and selectivity, and the background and artifact levels exhibited by these polyimides.

The DADS/PMDA polyimides made by solution polymerization in NMP and precipitated with either acetone or water showed reproducibly low (< 1 m^2/g) surface areas.

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